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RELATION OF PARTICLE SIZE AND CHARACTERISTICS OF LIGHT REFLECTED FROM PORCELAIN ENAMEL SURFACES*

By C. H. Zwermann and A. I. Andrews

Abstract

Various opacifiers were added in increasing percentages to clear, regular white, very opaque white, and acid-resisting enamels. These were ground to various degrees of fineness from coarse down to a few microns or finer; they were applied to sample plates and their reflectances were measured. Increased opacity is obtained by extremely fine milling because of the excellent dispersion of the opacifiers.

I. Introduction

(1) General

Porcelain enamels appear white because of finely divided transparent solid and gaseous occlusions in a clear, glassy matrix. The solid particles are undissolved material added either to the frit or to the mill batch or they are particles crystallized from the cooled glass. The gaseous occlusions are occluded air or decomposition products. A certain thickness, varying with the enamel, is required to produce maximum reflection of the incident light. Thinner coats appear gray because of the partial transmission of the light through the white layer and its subsequent absorption in the base metal or ground coat. If the suspended solid particles or glassy matrix show selective absorption, scattering, or reflection, the enamel will appear colored.

All of the properties of light, viz., reflection, scattering (sometimes referred to as Rayleigh scattering), absorption, refraction, and diffraction, help to produce opacity in enamels. Reflection, scattering, and absorption, however, are the most important factors. Light, in passing from a clear media of one index into that of another, is partially reflected at the interface. The amount is dependent on the original intensity of the incident light, the difference in indices of the two media, the angle of incidence of the light beam, and the area of the interface. Fresnel has developed formulas for calculating this reflectance.[1] If a curve for reflectance is plotted from a glass-air interface, the reflectance is shown to increase from 4% at normal incidence to 100% at glancing incidence for glass with an index of refraction of 1.5. Reflectance curves for glass-opacifier interfaces show that, for normal incidence, the reflectance from the glass-fluoride interface is less than 1%, about 2% for SnO_2-glass interfaces, and more than 6% for Sb_2O_3- and TiO_2-glass interfaces. For air-opacifier interfaces with normal incidence, the reflectance from fluorides is around 2%, glass 4%, SnO_2 11%, and ZrO_2, TiO_2, and Sb_2O_3 more than 16%. These data show that occluded gas is desirable and that the higher the index of refraction of the solid opacifier, the higher the reflectance at the interface. The percentage of opacifier giving the maximum number of interfaces with the glass should give the best reflectance, and the finer the opacifier, the greater the reflectance per unit of weight.

Rayleigh[2] and Mie[3] found that for particles up to one-third the wave length of light in diameter the light is uniformly scattered on both sides of the plane containing the particle and the normal to the incident beam. The intensity of the incident light returned in the direction of incidence increases as the square of the volume of the particle. The light sent out at right angles to the incident beam is totally polarized. Silberstein,[4] Shoulejkin,[5] Gans,[6] and Blumer[7] have found that for particles as large as one-third the wave length of light there is already a tendency for the light to be scattered in the forward direction. The rays in this direction have an intensity of 2.5 to 11 times greater than that in the opposite direction. Polarization is incomplete in this range, and it is displaced toward the direction of the transmitted rays. With particles larger than the wave length of light, the intensity in the forward direction increases rapidly until normal reflection and refraction are reached. This change is gradual, showing the close relationship between scattering, reflection, and refraction.[8] The foregoing applies to single particles far apart. If the spacing becomes too close, there will be destructive interference of the light from adjacent particles.

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* Based on thesis submitted by Carl H. Zwermann in partial fulfillment of the requirements for the degree of Ph.D. in Engineering, University of Illinois, June, 1939.

Revised copy received November 30, 1939.

[1] R. W. Wood, Physical Optics, 3rd ed. Macmillan Co., New York, N. Y., 1934; *Ceram. Abs.*, **13** [8] 205 (1934).

[2] Lord Rayleigh, "Transmission of Light Through an Atmosphere Containing Small Particles in Suspension, and Origin of the Blue of the Sky," *Phil. Mag.*, Series 5, **47** [287] 375–84 (1899).

[3] Gustav Mie, "Beiträge zur Optik trüber Medien, speziell Kolloidaler Metallösungen," *Ann. Physik*, Series 4, **25** [3] 377–445 (1908).

[4] L. Silberstein, "Transparency of Turbid Media," *Jour. Optical Soc. Amer.*, **15** [3] 125–30 (1927).

[5] W. Shoulejkin, "Scattering of Light by Very Big Colloidal Particles," *Phil. Mag.*, Series 6, **48** [284] 307–20 (1924).

[6] R. Gans, "Strahlungs Diagramme ultramikroskopischer Teilchen," *Ann. Physik*, Series 4, **76** [1] 29–38 (1925).

[7] H. Blumer, "Strahlungs Diagramme kleiner dielektrischer Kugeln," *Z. Physik*, **32** [May] 119–34 (1925); **38** [July] 304–28 (1926).

[8] F. A. Jenkins and H. E. White, Fundamentals of Physical Optics. McGraw-Hill Book Co., New York, N. Y., 1937.

Light passing through a medium gradually diminishes[9] in intensity because of absorption. This absorbed energy is transformed into heat, it is reemitted as fluorescent rays, or it produces a photochemical reaction. Absorption, within limits, is proportional to thickness. Enamels absorb some light, and it is only reasonable to expect a decrease in thickness to result in a decrease in absorption and to allow more light to be reflected. It is the actual light path and not the enamel thickness that must be considered.

For a given wave length of light and a material of a given index of refraction, the intensity of the reflected light will increase inversely as the diameter of the particles, and the intensity of the scattered light will increase as the third power of the diameter for a given weight of material. Thus, there is a size for each material at which it will give maximum opacity. Stutz and Pfund[10] have determined that the maximum opacity for ZnO, which has an index of refraction of 2.0, occurs with particles 0.24 micron in diameter with light which has a wave length of 0.54 micron. Bechhold and Hebler[11] have shown that the maximum opacity for $BaSO_4$, having an index of refraction of 1.64, occurs with particles 0.8 micron in diameter. The maximum opacity thus occurs in the range of particles whose diameters are of the order of the wave length of light.

(2) Review of Literature on Particle Size in Enamels

In 1922, Sweely and Prince[12] found that a variation in fineness of grinding produced a variation in the opacity of the enamel and that higher opacities were obtained with finer milling. They recommended grinding the enamel so that 5 to 10% would be retained on a No. 120 sieve. (A No. 120 sieve has an opening of 125 microns; a No. 200 sieve, an opening of 74 microns; and a No. 325 sieve, an opening of 44 microns.)

Figure 1 sums up all of the literature on fine milling. In 1935, Porter and Holscher,[13] milling to a fineness of 0.2% on a No. 325 sieve, obtained reflectances of 54% with a minimum application of 22 grams per sq. ft. In 1936, Bryant and Porter [14] obtained a reflectance of 58% with a minimum application of 20 grams per sq. ft. Tin oxide, added at the close of the milling period rather than at the start, gave enamels with higher reflectances. More than 12% mill additions of tin oxide did not increase the reflectance. Danielson[15] reports variations of 5% in the reflectance of enamels with variations in the type of clay used. The authors[16] obtained increased reflectances of colored enamels by finer milling of the enamels. Andrews and King[17] reported that finer milling of the enamel should increase the reflectance because of better dispersion of the mill-added opacifier. Late in 1938, instead of the customary 3 or 4% on a No. 200-sieve fineness for enamels, some frit companies were recommending finer milling. By grinding a certain enamel to a fineness of 1% on a No. 325 sieve and by adding 12% mill opacifier, reflectances of 62 and 72% were obtained with applications of 20 grams per sq. ft. and 34 grams per sq. ft., respectively.[18] A new enamel, ground to a residue of 1 gram on a No. 325 sieve, showed a reflectance of 66% at 20 grams per sq. ft. and 72% reflectance at 32 grams per sq. ft.[19] A manufacturer of opacifiers has recommended high mill additions of opacifier, viz., 20% with fine grinding and 1% on a No. 325 sieve to decrease the thickness of enamel required to give good opacity.[20] Reflectances of 66% were obtained with applications of 20 grams per sq. ft., and of 72% at about 26 grams per sq. ft.

(3) Purpose

The purpose of this work was to determine the effect of extremely fine milling on the reflectance of porcelain enamels. Although fine milling was known to increase the reflectance, no work had been done on this type of milling. Extremely fine milling also might possibly improve the enamels. Much thinner layers could be used, which would increase their resistance to chipping and scratching and thus improve adherence.

Maximum opacity should be obtained with one material suspended in another, when the suspended material is about the size of the wave length of light and the distance between the suspended particles is of the order of the wave length of light. For this condition, approximately 30 to 35% of suspended material and 65 to 70% of liquid would be necessary. The higher percentage of liquid is necessary to fill the voids, assuming that spherical particles are in the suspension. Enamel opacifiers (gas and solid) in suspension have a tendency to form clusters rather than to disperse. Extremely fine milling, therefore, offers one method to obtain better dispersion of the particles in the enamel glass, and the reflectivity of the enamel is more nearly approached with thinner layers. In

[9] G. W. Morey, Properties of Glass. American Chemical Monograph Series, Reinhold Publishing Corp., New York, N. Y., 1938; *Ceram. Abs.*, **18** [2] 48 (1939).

[10] G. F. A. Stutz and A. H. Pfund, "Relative Method for Determining Particle Size of Pigments," *Ind. Eng. Chem.*, **19** [1] 51–53 (1927).

[11] H. Bechhold and F. Hebler, "Nephelometric Effect in Colloid Systems of Different Particle Sizes," *Kolloid Z.*, **31** [2] 70–80 (1922).

[12] B. T. Sweely and E. S. Prince, "Relation of Fineness of Grinding to Opacity in White Enamels," *Jour. Amer. Ceram. Soc.*, **5** [12] 855–57 (1922).

[13] F. R. Porter and H. H. Holscher, "Use of Finely Milled Enamel Slips," *ibid.*, **18** [2] 39–42 (1935).

[14] G. L. Bryant and F. R. Porter, "Effect of Mill Practice and Mill Additions on Opacity of Enamels," *ibid.*, **19** [2] 55–59 (1936).

[15] R. R. Danielson, "Effect of Clays on Opacity of White Enamel for Sheet Steel," *ibid.*, **19** [2] 59–61 (1936).

[16] A. I. Andrews and C. H. Zwermann, "Fundamentals of Color in Porcelain Enamels," *ibid.*, **22** [3] 65–72 (1939).

[17] A. I. Andrews and B. W. King, Jr., "Mechanism of Mill-Added Opacity in Porcelain Enamels," *ibid.*, **22** [6] 173–76 (1939).

[18] "What About Fine Grinding," *Better Enameling*, **9** [12] 5–7 (1938).

[19] "New Ultra-Opaque Enamels," *Enamelist*, **16** [4] 5–10 (1939).

[20] W. V. Knowles, "Finely Milled, High Opacity Enamels," *Ceram. Ind.*, **32** [3] 52–56 (1939); also *Ceram. Age*, **33** [3] 72–73 (1939); *Ceram. Abs.*, **19** [3] 61 (1940).

addition to the cost, the practical amount of opacifier that may be added to the enamel is limited, owing to the fusibility of the enamel.

Extremely fine milling increases the exposed surface enormously and results in greater base-exchange capacity and probably in greater solubility. A greater quantity of water is needed to suspend the enamel frit normally, and higher shrinkage tendencies, which accompany higher water content, cause a defect known as "tearing." By the use of liquids, which have a lower dipole moment[21] than water, it was hoped to remedy this defect.

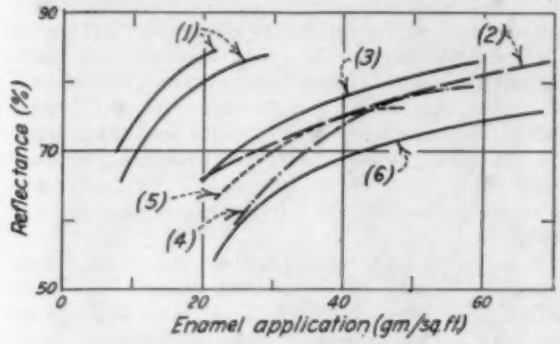

FIG. 1.—Reflectance curves: *curve* (*1*) work of present authors; (*2*) see *Enamelist*, footnote 19; (*3*) W. V. Knowles, footnote 20; (*4*) Bryant and Porter, footnote 14; (*5*) *Better Enameling*, footnote 18; (*6*) Porter and Holscher, footnote 13.

II. Experimental

Two 45-pound batches of each enamel were smelted in a rotary furnace at 2000°F. The batch compositions were as follows:

Batch composition	Enamel No. (1)	(2)	(3)	(4)
Feldspar	40.4	22.80	9.50	17.60
Flint	18.1	21.13	39.00	23.47
Borax	28.0	23.07	18.00	22.88
Soda ash	3.8	6.34	10.00	6.70
Soda niter	2.2	2.96	3.00	2.93
Fluorspar	3.2	3.38	1.50	2.51
Cryolite	2.3	10.14		8.38
Zinc oxide		3.38		2.93
Sodium antimonate		6.76	9.50	12.58
Sodium silicofluoride			5.00	

Enamel No. 1 is a typical clear enamel used for colors; Nos. 2, 3, and 4 are regular white, acid-resisting, and very opaque white frits, respectively, identical in composition to some used by the National Bureau of Standards.[22]

Five 100-gram batches were made up of the No. 1 clear frit, with varying percentages of clay or bentonite; tin oxide, Opaline,[23] Opax, or titanium oxide, as the opacifier; and with various liquids, such as kerosene, turpentine, turpentine with Damar varnish; methyl, ethyl, butyl, and propyl alcohols; or distilled water, as the suspending media. These batches were ground for sixteen hours in small laboratory ball mills. Enough liquid was added to each batch to give a consistency equal to that of cream. The enamels were screened through a No. 325 sieve and were passed twice through a Premier colloid mill, operating at 17,000 r.p.m., with the disks set 0.002 inch apart. Test pieces, 4 by 4 inches, of various kinds of iron, such as ground-coated, nickel-dipped, sand-blasted, oxidized, pickled, and crude, were sprayed with light coats and were fired in an electric furnace for three minutes at 1500°F.

The best results were obtained with water as the suspending medium, bentonite for dry strength, and either Opaline, titanium oxide, or tin oxide as the opacifier. These materials were used in additional tests. The enamels, prepared as described, were sprayed on the 4- by 4-inch ground-coated, sheet-iron pieces. Ratios of 0 to 1.3 parts of opacifiers to 1 part frit were used. The firing time was varied from 3 to 4 minutes, and the temperatures were 1500° to 1800°F. to obtain the best gloss.

Tearing occurred in the pieces that contained high percentages of opacifiers. An addition of 0.5% $NaNO_2$ prevented tearing and improved the gloss remarkably. Applications of 20 grams per sq. ft. of frit to a ratio of opacifier greater than 1 to 0.6 did not increase the reflectance materially. A microscopic examination of the enamel slip showed most of the frit particles to be only a few microns or smaller in size and a few particles as large as 30 microns. The latter were larger than was desirable and it was thought that the reflectance would be improved materially by their elimination.

Fractionations of the milled No. 1 clear frit were made by allowing the ground material to settle in water for two hours and by removing the top 10 cm. Concentrations of four parts by weight of frit to 96 parts water were used. A microscopic examination showed most of the particles to be below 5 microns in size. The frit was dried, and 150-gram batches were mixed with water for one hour in small laboratory ball mills with varying additions of opacifiers and suspending agents. The enamel was sprayed on 4- by 4-inch ground-coated sample pieces and dried at room temperature. Tearing occurred, especially on the heavier coatings, although it was minimized by the addition of bentonite and $NaNO_2$. The addition of 10% of a coarser fraction of frit eliminated the tearing, but this was getting away from the extremely fine milling that was sought. The soluble salts were concentrated in the finest fraction with water fractionations, and this seemed to increase the tearing. The fractionation should be made in air or in some liquid in which the frit is not so soluble.

[21] Erhard Gruner, "Adsorptionssysteme von Kaolin und Tonen mit Flüssigkeiten im Zusammenhang mit der Erscheinungen der Plastizität," *Z. anorg. allgem. Chem.*, **215** [1] 1–18 (1933); *Ceram. Abs.*, **13** [4] 101 (1934).

[22] W. N. Harrison, R. E. Stephens, and S. M. Shelton, "Consistency of Eight Types of Vitreous Enamel Frits at and near Firing Temperatures," *Jour. Research Nat. Bur. Stand.*, **20** [1] 39–55 (1938); R.P. 1063; *Ceram. Abs.*, **17** [4] 134 (1938).

[23] Opaline is a ceric oxide opacifier, made in France and used considerably in Europe. See H. Melzer, "Opacifiers in Wet and Powder Enamels," *Glashütte*, **67** [34] 530–32 (1937); *Ceram. Abs.*, **17** [2] 57 (1938).

Roller [24] has developed an apparatus for the fractionation of dry materials down to 0 to 5 microns in diameter, but this equipment is not suitable for handling large quantities of material. Commercial separators may also be used for fine fractionations, but it is difficult to get clean separations of the finest fractions.

Twenty pounds of each frit were milled dry and the powdered materials were fractionated with a laboratory classifier.* Each frit was passed five times through the classifier, with the air opening set at 2 inches and the mesh at $^5/_{16}$ inch, and two times with the air opening set at 2 inches and the mesh at $^{13}/_{16}$ inch. This gave two fractions in addition to the rejects. Most of the fines of the first fraction were under 4 microns, although a few particles were as large as 10 microns. The particles in the second fraction were chiefly under 12 microns with a few up to 20-micron-fines. Although these fines were coarser than desired, they were used in all of the fine milling tests which follow.

Even with mill additions of 5% of bentonite and 0.5% of $NaNO_2$ to which electrolytes, such as HCl, sodium silicate, sodium carbonate, and tannic acid, were added, tearing occurred in the fired enamels, both with slow and fast drying. The clear No. 1 frit showed the greatest amount of tearing. If, however, the frit could be "preshrunk" in some manner, it was thought that this defect might be eliminated.

The frits were milled wet in a ball mill with various percentages of opacifiers, dried, passed through a No. 20 sieve, and then heated in fire-clay crucibles in an electric furnace at temperatures varying from 900° to 1400°F. These frits did not cause tearing in the enamel when they were heated sufficiently. It was unnecessary to fuse them completely. Some shrinkage occurred, but the material was still friable.

With a standard composition of 100 parts of frit and opacifier, 5% of bentonite, 0.5% of $NaNO_2$, and 100 to 130% of water, batches of coarse-milled and fine-milled enamels were prepared, using all four types of frit and varying percentages of such opacifiers as Opaline, tin oxide, titanium oxide, Treopax, Opax, sodium antimonate, and antimony oxide. A few batches with red, blue, or green stain were also prepared. The 500-gram batches of the quenched frit and mill additions were milled to 1% fineness on a No. 200 sieve or to 1% on a No. 325 sieve by the Standard Method for Fineness.[25] The 150-gram batches of the fine fractions of the four frits were milled with the opacifiers to insure a good mixture. They were then dried, passed through a No. 20 sieve, heated in refractory crucibles to 1000°, 1150°, or 1400°F., mixed wet with the proper mill additions for 1 hour in ball mills, and sprayed on the 4- by 4-inch ground-coated sample pieces. The pieces were dried at room temperature and were brushed, leaving an area of covered surface equal to 12 square inches. All enamel applications were weighed to $^1/_{100}$ gram, and the application was expressed in grams per square foot, the term used in commercial practice. At least four pieces were sprayed with each enamel to a thickness of 8 to 25 grams per sq. ft. so that the reflectance curves could be plotted. Pieces of crude, pickled, nickel-dipped, and oxidized sheet iron were also sprayed as a check on the characteristics of the enamel used on such pieces. Most of the enamels were fired at the standard temperature and time, viz., at 1500°F. for three minutes, but a few were given a shorter heat treatment.

Thickness measurements were made on several pieces with a General Electric electric thickness gauge.

Reflectance measurements for green, blue, and amber filters and for specular gloss measurements were made on each piece with a Hunter multipurpose reflectometer. All pieces were refired for the same length of time and at the same temperatures as the first firings, and the reflectance measurements were repeated. Reflectance curves were drawn for most of the enamels to show comparisons of the frits, opacifiers, and fineness of milling.

A microscopic examination of several of the fines, opacifiers, enamel slips, and fired enamels was made with a Leitz ultrapak microscope at magnifications up to 1000×. Thin sections of several of the enamels were examined under reflected and transmitted light, and photomicrographs were taken of some of the sections.

Additional work was done on thin applications of extremely fine-milled ground coats and on the use of titanium oxide in extremely fine-milled white cover-coats.

III. Results and Discussion

Corresponding fractions of all frits seemed to contain the same size and distribution of particles. The Opaline, tin oxide, and titanium oxide particles were 1 or 2 microns in size or smaller; titanium oxide, however, was the smallest and Opax the coarsest. Photomicrographs (2), (3), and (4) in Fig. 2 show the different frit fractions, and (5) shows the Opaline.

Considerable shrinkage occurred during the preheating of the enamel frit with the opacifier before there was sufficient fusion to prevent the agglomerate from being broken up. The best temperature for heating varied with the composition of the frit and the amount and kind of opacifier added. The clear frit, which showed the greatest amount of tearing, should be well "preshrunk." The other frits, which did not reveal as much tearing, might not need preheating. The shrinkage is due to the rounding of the corners of the particles and the fusion of the extremely small particles. This reaction is valuable in two ways because it allows closer packing and also decreases the surface area and its accompanying solubility.

In spraying, the water content was varied so that the enamel would smooth down when it was applied. Lower air pressures, viz., less than 40 lb. per sq. in., gave the best results. The high bentonite content aids materially in the adherence of the dry enamel to the ground coat. It also requires more water to render the enamel

[24] P. S. Roller, "Separation and Size Distribution of Microscopic Particles: Air Analyzer for Fine Powders," *Bur. Mines Tech. Paper*, No. 490, 46 pp. (1931); *Ceram. Abs.*, **10** [6] 448 (1931).

* Federal Pneumatic Systems, Inc., made these fractionations.

[25] "Report of Enamel Division Standards Committee, 1930," *Bull. Amer. Ceram. Soc.*, **9** [9] 269–71 (1930).

fluid, and it permits a larger amount of wet enamel to be applied and still maintain a low dry weight per unit of area. Not much difference was noted between the pieces placed in a drier and those dried at room temperature. A few of the enamels shorelined when they were dried too slowly.

Photomicrographs (6), (7), and (8) in Fig. 2 show a regular two-coat white enamel and two extremely fine-milled enamels, one with 9% of mill-added opacifier and the other with 40% of opacifier. Their reflectances are 73.0, 74.8, and 76.0%, respectively.

The reflectance curves in Fig. 3 are shown for clear

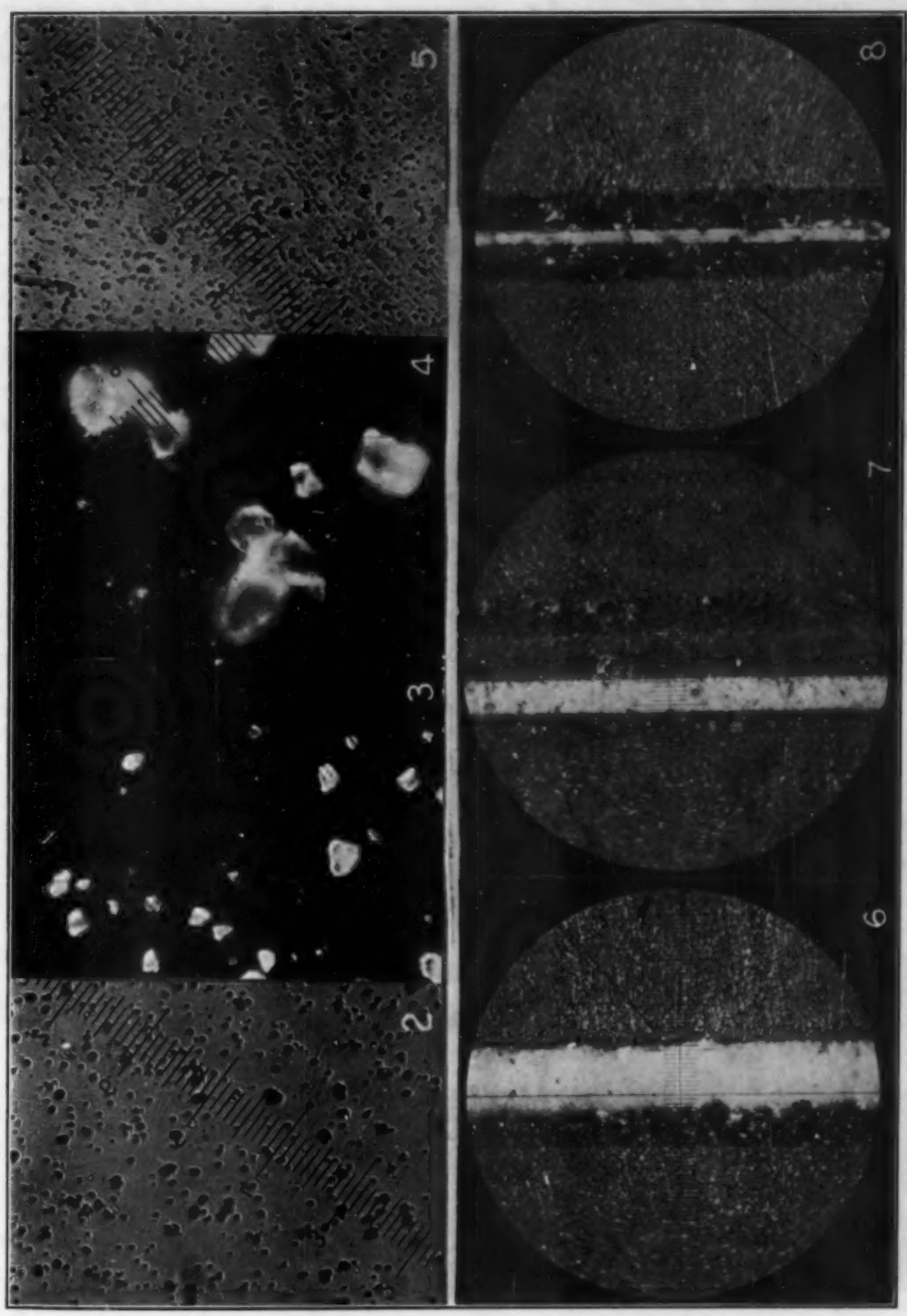

FIG. 2.—*Photomicrograph No.* (2) No. 1 frit, first fraction; (3) No. 1 frit, second fraction; (4) No. 1 frit, rejects; (5) Opaline; (6) regular two-coat superopaque white, 55 gm. per sq. ft.; (7) one-coat white, clear frit plus 10% Opaline, 21½ gm. per sq. ft.; (8) one-coat white, clear frit 40% Opaline, 10.9 gm. per sq. ft.

No. 1 enamel without mill-added opacifiers. With applications of 20 grams per sq. ft., fine milling increases the reflectance from 15 to 26%, chiefly owing to the decrease in the size of the gas bubbles present in the enamel, which gives a greater area of air-glass interface. Photomicrographs (10) and (11) in Fig. 2 show thin sections, respectively, of the coarse and extremely fine-milled enamels. Each scale division equals 3.2 microns. In the coarse-milled enamel, the bubbles are 35 microns and smaller, whereas in the fine-milled enamels they are 5 microns and smaller. This clear enamel has quite a low viscosity. The firing time and temperature must be maintained; if they are overfired, the bubbles increase in size and decrease in number (see photomicrograph (12) in Fig. 2). This enamel is the same as (11), but it was fired harder. The gas bubbles in (12) are 15 microns and smaller and are caused by occluded air or by decomposition products. In the case of occluded air, the finer grinding produces smaller interspaces but a greater number of them. In the latter case, gas bubbles occur during the decomposition of the high bentonite addition.

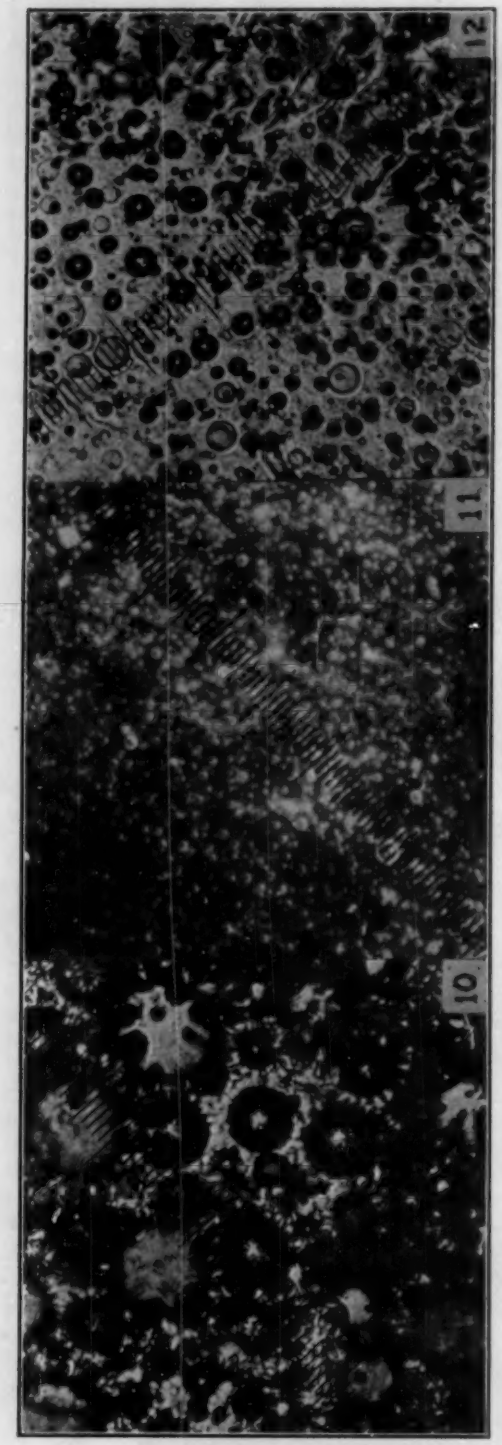

FIG. 2 (*concluded*).—*Curve* (*10*) coarse-milled clear enamel, 1% on No. 200 sieve; (*11*) extremely fine-milled clear enamel; and (*12*) extremely fine-milled clear enamel, overfired.

Figure 3 also shows an increase of reflectance with additions of 5, 10, 15, 20, and 30 parts of Opaline. A small addition of Opaline increases the reflectance tremendously, and with fine milling this increase is even greater. Good enamels with a reflectance of more than 70% may be obtained with applications as low as 10 grams per sq. ft. of 20 to 30% of Opaline.

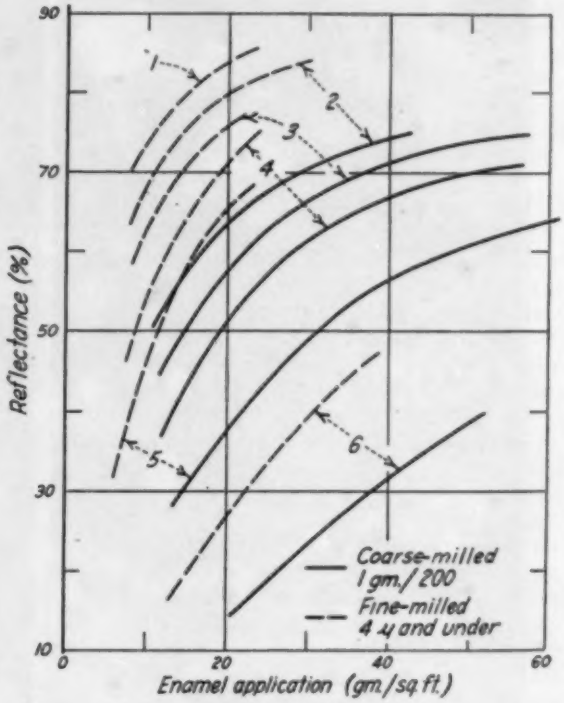

FIG. 3.—Variation of reflectance with thickness of coarse- and fine-milled clear enamel frit with different percentages of Opaline.

	No. 1 frit	
Curve No.	(%)	Opaline (%)
(*1*)	70	30
(*2*)	80	20
(*3*)	85	15
(*4*)	90	10
(*5*)	95	5
(*6*)	100	0

Reflectance curves of the extremely fine-milled enamels seem to approach a much higher limit than those of the coarse- or normal-milled enamels, which may be accounted for by the increase in reflectance owing to less absorption.

Figure 4 shows the effect of the degree of frit fineness on the opacity, viz., that fine milling is extremely helpful in increasing the reflectance of thin coatings.

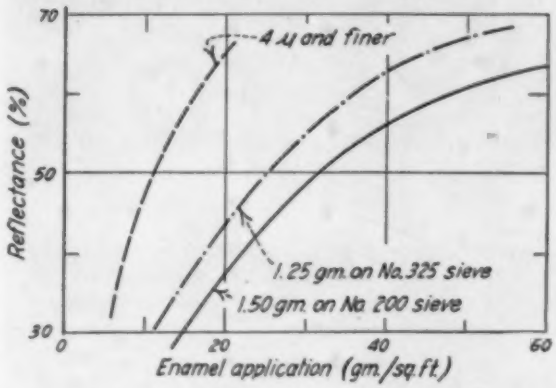

FIG. 4.—Variation of reflectance with fineness of milling of clear enamel frit with 5% Opaline.

Figure 5 shows the amount of reflectance when blue and amber filters are used in fine- and coarse-milled enamels (with Opaline as an opacifier) for the regular fire and a refire at the same time and temperature. The change in reflectance after refiring was negligible, which reveals the long firing range of these enamels.

The use of tin oxide as an opacifier gave similar results. Figure 6 shows the action of titanium oxide, which differs from the results in Fig. 5. After the coarse-milled enamels were refired, the reflectance drops off rapidly, especially with the heavier coatings, and the enamels have a definite yellow color. This color has been reported to be caused by the change of anatase to rutile. With the extremely fine-milled enamels, the reflectance does not change so rapidly after refiring, and a good white is obtained. The inversion of the anatase to rutile has been retarded.

Figure 7 shows the relative opacifying power of the different opacifiers; Opaline and titanium oxide are the best, tin oxide is good, and the other opacifiers are not quite so good. In all cases, finer milling increases the reflectances tremendously.

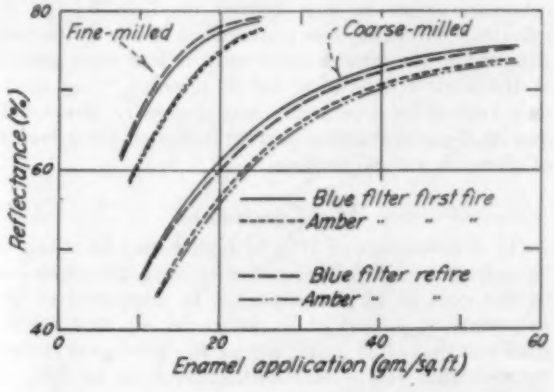

FIG. 5.—Variation of reflectance using blue and amber filters with refired fine- and coarse-milled clear enamel frit and 15% Opaline (fired and refired at 1500°F. for 3 minutes).

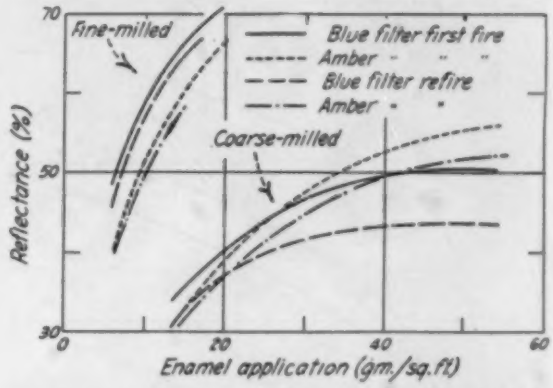

FIG. 6.—Variation of reflectance using blue and amber filters with refired fine- and coarse-milled clear enamel frit and 10% titanium oxide (fired and refired at 1500°F. for 3 minutes).

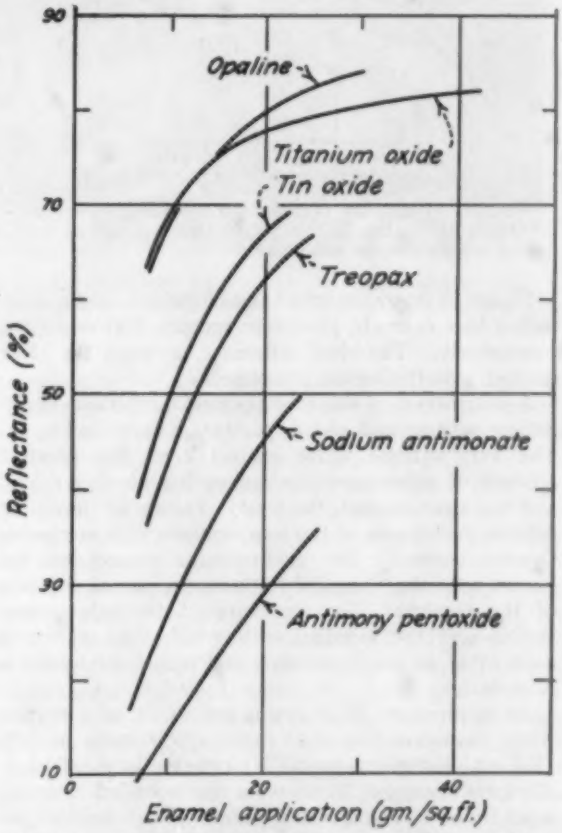

FIG. 7.—Variation of reflectance with thickness of fine-milled, clear enamel frit with various opacifiers (80% No. 1 frit and 20% opacifier).

Figure 8 shows the rapid rate at which the reflectance of the clear enamel increases with small additions of Opaline as compared with tin oxide and Opax.

The reflectance of fine- and coarse-milled blue and red enamels is shown in Fig. 9. The extremely fine-milled enamels have much greater reflectance, and it is possible to obtain brighter colors.

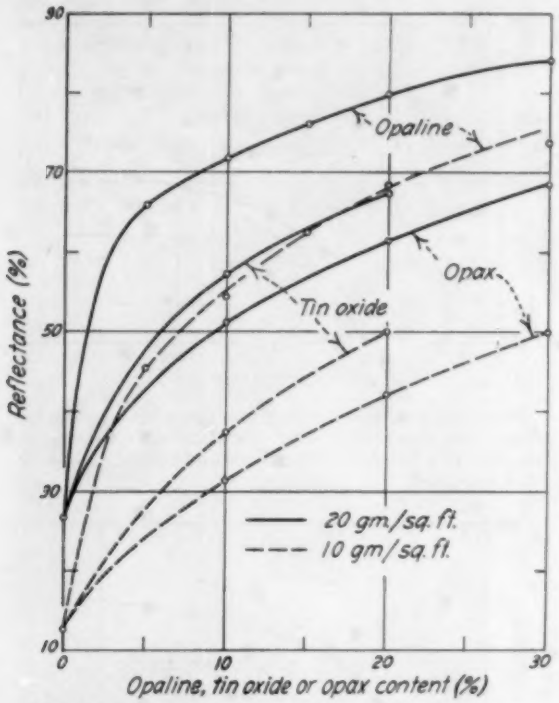

FIG. 8.—Variation of reflectance with various percentages of Opaline in fine-milled clear enamel as compared with tin oxide and Opax.

Figure 10 shows the structures of the fine- and coarse-milled blue enamels, photomicrographs (19) and (20), respectively. The chief difference, as with the clear enamel, is in the bubble structure.

A comparison of the four enamels for various applications without mill-added opacifiers is shown in Fig. 11. The very opaque white enamel gives the greatest amount of reflectance; the succeeding ones give less; and the clear enamel, the least. Figure 12 shows the relative reflectance of the four enamels with increasing Opaline content. The acid-resisting enamel has the lowest reflectance, probably owing to partial solution of the Opaline. The similarity of the other three curves and the rapidity with which they approach each other as small amounts of Opaline are added is remarkable.

An application of 55 grams per sq. ft. of a regular white enamel in two coats shows a reflectance of 72% (Fig. 10, photomicrograph (24), note the large bubbles). Photomicrograph (23) shows a coarse-milled clear enamel frit with 10 parts of Opaline. Large bubbles are present. With finer milling, these bubbles are absent; the enamel is more opaque, like the structure between the large bubbles in the coarse-milled enamel.

When the enamel was applied directly on iron, the best results were found with the clear frit which contained about 5% of Opaline. The impact test showed that the adherence was not so good on pickled steel as on regular cobalt ground coat, but when it was applied on iron oxidized at 1000°F. for five minutes, it was comparable. The iron in most cases had to be de-

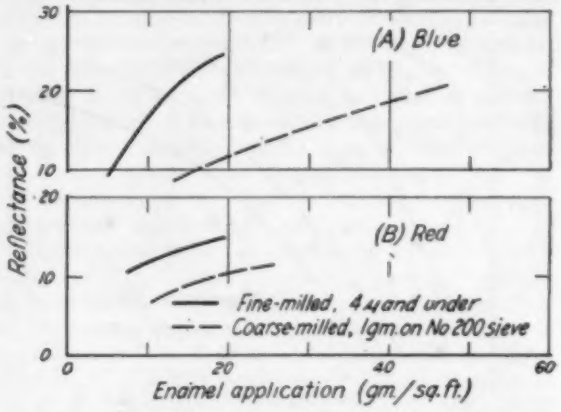

FIG. 9.—Variation of reflectance with thickness of coarse- and fine-milled clear enamel frit with 5% of blue or red stain.

formed to chip the enamel. Melzer and Budweis[23] recommend the use of cerium oxide in ground-coat enamels. This work shows it to be helpful in fine-milled enamels. By milling the ground coat extremely fine, it was possible to apply it successfully by spraying at a thickness of less than 0.002 inch. The substitution of bentonite for clay eliminated any tendency of tearing.

Good results were obtained with further tests on the use of titanium oxide. A reflectance of 74% was obtained when 10 grams per sq. ft. of enamel, with 80 parts of clear frit and 20 of titanium oxide, were applied. With two refirings at 1500°F. for 3 minutes each, the reflectance dropped only 2%, and the enamel retained its whiteness. A titanium oxide enamel, milled extremely fine, showed a slight creamish discoloration after it was heated at 1500°F. for 10 minutes. No rutile was apparent in X-ray diffraction patterns of the same enamel until it had been heated at the same temperature for 20 minutes. One specimen heated for five hours was decidedly discolored, and its X-ray diffraction pattern indicated the presence of all rutile and no anatase.

IV. Conclusions

(1) A reflectance of 70% or higher may be obtained by extremely fine milling and with applications as low as one coat of 10 grams per sq. ft. compared to the two coats, e.g., that of 55 grams per sq. ft. formerly used and that of 35 grams per sq. ft., which was recommended this year. Mill additions of 20 to 25% of opacifier are advantageous.

(2) The increased reflectance is due to the increased interfaces of opacifier and frit and to the increase in the number and the decrease in the size of the gas bubbles.

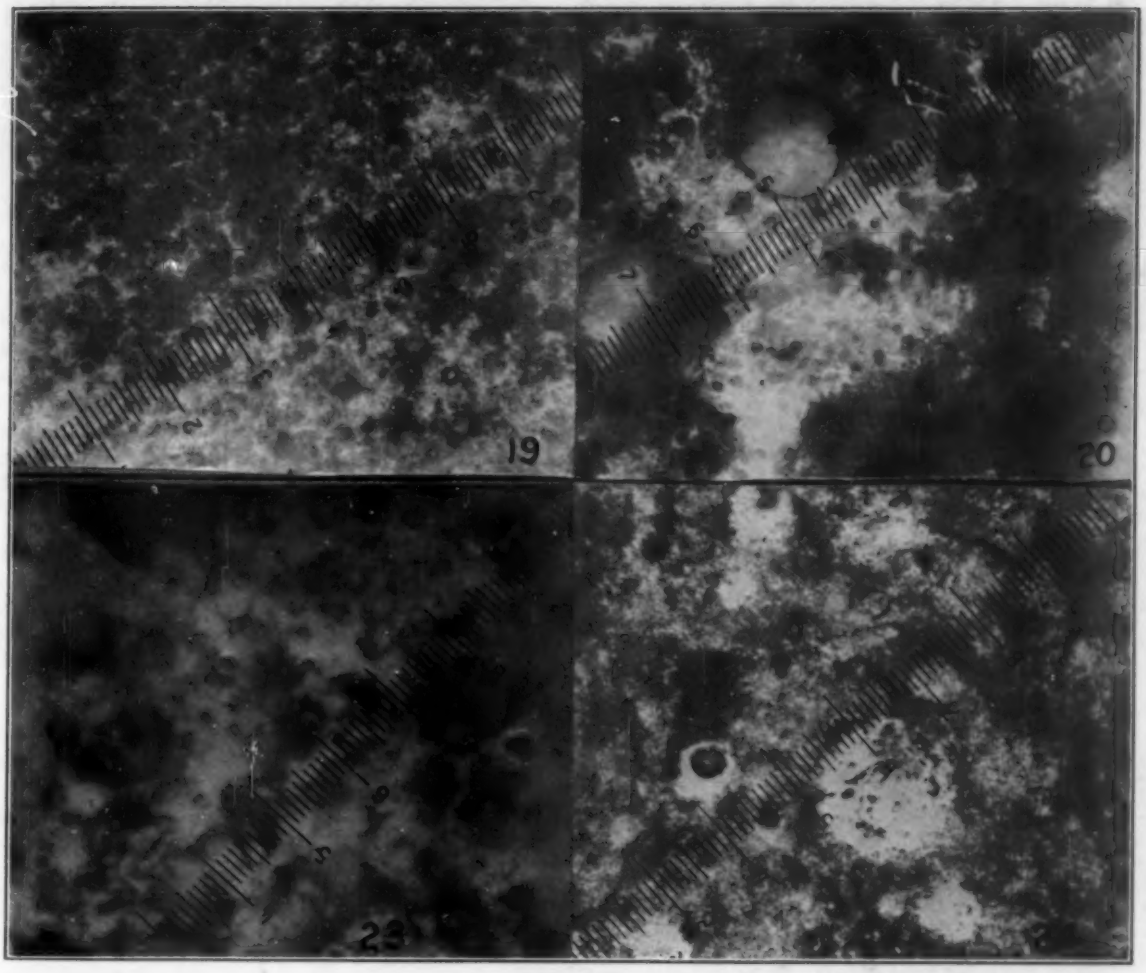

FIG. 10.—*Photomicrograph* (*19*) extremely fine-milled clear enamel with 10% blue stain; (*20*) coarse-milled clear enamel with 10% blue stain, 1 gm. on No. 200 sieve; (*23*) regular white enamel, 4 gm. on No. 200 sieve, applied 55 gm. per sq. ft.; and (*24*) clear enamel with 10 parts Opaline, 1 gm. on No. 200 sieve.

The latter factor is important because of the greater relative difference in the indices of refraction of the gas and of the enamel constituents. Part of the increase in reflectance may be attributed to the decrease in absorption of the thinner coating of the fine-milled enamels, which allowed a greater amount of the light to be reflected.

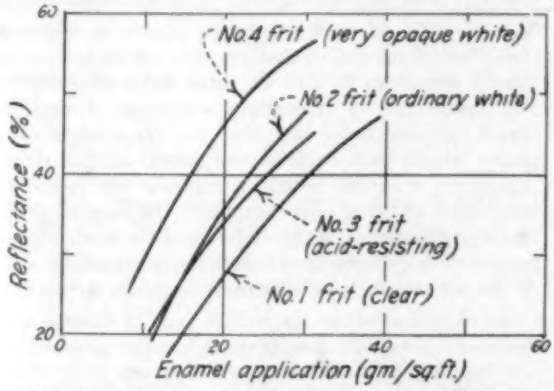

FIG. 11.—Variation of reflectance with thickness of different types of fine-milled enamel frits without mill-added opacifiers.

(3) The present method used to obtain a good distribution of the opacifier is more advantageous than other methods because there is less chance for solubility or aggregation.

(4) Extremely fine-milled enamels mature at a lower temperature than coarser fractions.

(5) Additions of bentonite and of $NaNO_2$ and preheating the enamel frit with the opacifier to promote shrinkage are helpful in eliminating tearing.

(6) Ground coats should be milled finer to decrease the size of the gas bubbles. The use of cerium oxide in fine-milled clear enamel, possibly on oxidized iron, may entirely eliminate the use of the ground coat. This offers a great opportunity for future work.

(7) Extremely fine-milled enamels are less easily scratched because of the smaller bubbles in the structure.

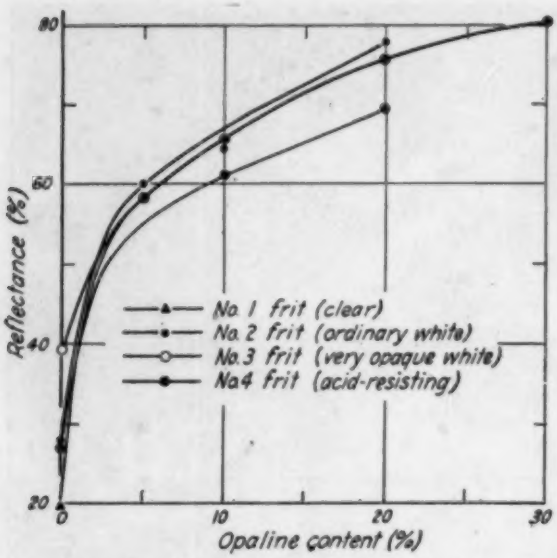

FIG. 12.—Variation of reflectance with increasing Opaline content in various fine-milled enamel frits applied 15 gm. per sq. ft.

(8) The adherence problems of extremely fine-milled enamels are different from those of the ordinary enamels.

(9) The use of extremely fine-milled enamels with colors gives more stable and brighter colors with a much lower percentage of additions of inert color stains.

(10) The use of clear frit is recommended in extremely fine-milled enamels because practically the same opacity is obtained as with very opaque frit.

(11) Titanium oxide and cerium oxide give the best opacity to the enamel.

(12) Closely allied with extremely fine grinding of enamels would be extremely fine grinding of some types of glazes for the glaze probably could be applied much thinner and there would be less likelihood of crazing.

(13) The enamels may be ground fine, either wet or dry. The dry process was used in most of this work so that a better comparison of the different enamels could be obtained.

DEPARTMENT OF CERAMIC ENGINEERING
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

SOME ASPECTS OF THE SCUMMING PROBLEM*

BY G. H. SPENCER-STRONG AND L. J. MCMAHON

ABSTRACT

The two general types of scumming and their causes are discussed. The sulfate type of scumming is caused by sulfates either in the enamel materials or in the atmosphere to which the ware is exposed. Nonsulfate types of scums are usually caused by a combination of factors, which include underfiring, excess water vapor in the furnace atmosphere, fineness of grinding, and mill additions, especially clays and opacifiers.

I. Introduction

Scumming is one of the most annoying defects encountered by the average sheet-steel enameler. Scum due to sulfates has long been known and widely commented upon in the literature, but a second type of scumming has been encountered recently in an increasingly large number of enameling plants, which results from a combination of factors entering into the enameling process.

The eradication of the nonsulfate type of scumming is considerably more difficult than the sulfate scum because usually there are several contributing factors. The summer of 1938 was marked by the prevalence of unusually hot, humid weather throughout most of the United States, and at the same time the production schedules of most enameling plants were considerably below normal so that operators were attempting weekly schedules in two or three days of operation. The prevalence of nonsulfate scumming during this period was unusually high and was reported in many plants which have seldom complained of this defect. Scumming was also noted on enamels which had the reputation of being nonscumming. In view of the increasing prevalence of this defect and the contradictory nature of the information received from the field, study of the nonsulfate type of scumming was undertaken.

Additional study of the sulfate type of scum was unnecessary because it has been thoroughly investigated and reported in the literature. A review of the literature and general comments only are given on this subject.

* Presented at the Forty-First Annual Meeting, American Ceramic Society, Chicago, Ill., April 18, 1939 (Enamel Division). Received August 11, 1939.

(1) Literature and General Considerations

Sulfate type scums, as the name implies, are due to the deposition of a white, nonvitreous layer of a sulfate material on the surface of the enamelware during or after the firing process. Andrews[1(a)] has shown that sulfate scum may be composed of a mixture of various alkaline sulfates and may be identified by scraping some of the material from the enameled sheet, dissolving it in water, and adding a few drops of barium chloride solution. If the scum is a sulfate type, a dense white precipitate of barium sulfate will be formed. Andrews and numerous other investigators[1] have shown that minute traces of sulfur in combustion gases which come in contact with ware because of a leaky muffle or other causes will give rise to this type of scumming. In fact, the sulfur dioxide present in the atmosphere of certain industrial districts is sufficient to cause sulfate scumming. Sulfates in raw materials, such as electrolytes and especially in coloring oxides of the cadmium sulfide type, may promote scumming.

A further and even more distressing cause of the sulfate scum arises from the exposure of finished enamelware to atmosphere in which there is a considerable amount of sulfate. For example, in storing enameled products, the smoke from industrial districts and locomotives must not be allowed to come in contact with the ware.

The storage of porcelain enamel refrigerators of types using sulfur dioxide as a refrigerant sometimes gives rise to scumming because of leaks in the refrigeration system. Fumes from pickle-room tanks where sulfuric acid is used may also cause this type of scumming. In one case, it has been reported that pickle-room fumes, i.e., those which were carried out of the closed pickle room through a ventilator, traversed the entire length of the building over the roof, were blown into a window at the far end of the building, and caused bad scumming.

Although the sulfate type of scum is a nuisance and is expensive, its cause may be rather easily discovered. Gummed bindings used on enamelware prevent the penetration of the scum, and laboratory experiments show that the application of certain synthetic resins will also protect the ware from this defect. The complete painting of large enameled pieces with such materials would be unduly expensive, but the black or dark portions of the ware, which show the scum most readily, could thus be coated.

There is only brief mention in the literature of a nonsulfate type of scum. Geisinger and Berlinghof have reported[1(i)] a frosting-like appearance on the surface of the enamelware that has been fired in atmospheres which have a high moisture content. McIntyre[1(e)] states that theoretically the scum may be due to the reaction of fluorine gases coming from the enamel, with the moisture in the furnace atmosphere giving rise to the formation of hydrofluoric acid which attacks the enamel and leaves a siliceous crust on the surface.

The studies of McIntyre and his colleagues[1(e)] on the influence of furnace gases on porcelain enamel defects do not show scumming to be the result of furnace atmosphere conditions.

In his study of the effect of soluble salts formed during aging on the scumming of enamels, Whitesell[2] found the increase of soluble salts with aging to decrease the scumming tendency, and when the temperature was increased to over 100°F., the greatly increased amount of soluble salts further decreased the scumming tendency.

II. Method of Procedure

The present investigation was actually carried out in three parts, viz., (1) an introductory survey of the problem, (2) a field investigation in which the results of the laboratory work were compared with facts discovered in the field, and (3) a second laboratory investigation covering those phases of the work which the preliminary survey and the field survey showed to be pertinent.

To simplify the present paper, the results of the laboratory investigations have been combined and those of the field investigation are appended in the form of a comparison of the laboratory results with the field results.

A study of reports from the field indicate that several factors are involved in the scumming complaints, but the chief contributing causes seem to be overloaded, continuous furnaces with a considerable temperature variation, high humidity, and combinations of certain clays and opacifiers.

Preliminary experiments showed that the nonsulfate-type scumming could be readily produced in the laboratory. An enamel fired in the middle of the furnace where it was subjected to uniform heating might not

[1] (*a*) A. I. Andrews, Enamels, pp. 301, 302, 372. Twin City Printing Co., Champaign, Ill., 1935; *Ceram. Abs.*, **14** [6] 158 (1935).
(*b*) A. I. Andrews, "Enamel Defects Due to Combustion Gases," *Enamelist*, **7** [8] 11–12 (1930); *Ceram. Abs.*, **9** [12] 1026 (1930).
(*c*) A. I. Andrews and E. A. Hertzell, "Progress Report on Effect of Furnace Gases on Quality of Enamels," *Jour. Amer. Ceram. Soc.*, **13** [8] 522–29 (1930).
(*d*) A. I. Andrews and E. A. Hertzell, "Effect of Smelter Atmospheres on Quality of Enamels for Sheet Steel," *Univ. of Ill. Eng. Expt. Sta. Bull.*, No. 224 (1931); *Ceram. Abs.*, **10** [9] 628 (1931).
(*e*) G. H. McIntyre, "Influence of Furnace Gases on Porcelain Enameling," *Enamelist*, **14** [4] 6–10 (1937); *Ceram. Abs.*, **16** [6] 169 (1937).
(*f*) H. E. Ebright and G. H. McIntyre, "Effects of Water Vapor on Porcelain Enamel During Firing," *Enamelist*, **10** [6] 11–13 (1933); *Ceram. Abs.*, **12** [8] 293 (1933).
(*g*) H. E. Ebright, G. H. McIntyre, and J. T. Irwin, "Study of Furnace Atmospheres and Temperature Gradients and Their Effect on Porcelain Enameling," *Jour. Amer. Ceram. Soc.*, **18** [10] 297–302 (1935).
(*h*) J. T. Irwin, "Checking Furnace Firing Conditions," *Enamelist*, **12** [4] 18–19 (1935); *Ceram. Abs.*, **14** [4] 87 (1935).
(*i*) E. E. Geisinger and K. Berlinghof, "Effect of Furnace Gases on Glass Enamels," *Jour. Amer. Ceram. Soc.*, **13** [2] 126–42 (1930).
(*j*) Discussion on "Effect of Muffle Atmosphere on Firing Enamels," *Bull. Amer. Ceram. Soc.*, **3** [11] 437–42 (1924).
(*k*) H. Heimann, "Small Causes, Large Effects," *Céram., Verrerie, Émail.*, **2** [3] 121–22 (1934); *Ceram. Abs.*, **14** [8] 183 (1935).

[2] R. J. Whitesell, "Effect of Soluble Salts Formed During Aging on Scumming of Enamels," *Jour. Amer. Ceram. Soc.*, **20** [3] 72–75 (1937).

scum, but the same enamel applied on the test piece and fired with one edge adjacent to the furnace door so that a temperature differential of approximately 100°F. existed between the two ends of the plate produced a noticeable scum at the colder end of the plate. This method of firing was followed throughout the investigation and will be referred to as "differential firing."

Throughout the investigation, standard 6- by 8-inch, 18-gauge enameling iron sample plates were used. Cover-coat enamels were ground to 7% fineness on 200-mesh and were applied at 50 grams per sq. ft., except where otherwise noted. Differential firing was conducted in an electric laboratory furnace.

The general mill formula used throughout the study was as follows:

	(lb.)
Frit	100
Clay	8
Opacifier	2
Magnesium carbonate	1/4
Water	38

Except as noted, two frits, a superopaque frit, A, and an opaque frit, B, and crude German Vallendar clay were used.

III. Results

(1) Frits

The scumming tendencies of seven nonacid-resisting and one acid-resisting cover-coat enamel of the opaque and superopaque types were determined, and the effect of the use of crude and refined clays was noted. The behavior of the individual frits with the two clays differed markedly with the exception of one frit which showed little or no scumming with either clay. A wide range of scumming between the different frits was noted. A comparison was made of the fluorine content of seven commercial enamel frits, ranging from clear glass to superopaque enamel, and of the Na_2O content and B_2O_3 and Na_2O ratios of their mill liquors with their scumming tendencies. The enamels were milled with 6% German Vallendar clay (clay No. 10, Table IV). Table I shows the results of this test.

TABLE I

EFFECT OF FLUORINE CONTENT OF FRITS AND OF Na_2O AND Na_2O/B_2O_3 CONTENT OF MILL LIQUORS ON SCUMMING

Frit No.	Type	F_2	Na_2O (ml./l.)	B_2O_3/Na_2O	Scum (mm.)	Humidity (lb. H_2O/ lb. dry air)
1	Clear	0.87	1.16	1.58	122	0.012
2	Clear	2.11	1.80	1.35	110	.012
3	Opaque	7.20	1.76	1.32	95	.012
4	Opaque	7.10	2.42	1.19	70	.012
5	Opaque	5.19	1.95	1.24	40	.012
6	Superopaque	7.75	2.05	1.05	95	.012
7	Superopaque	6.72	2.27	1.22	115	.012

No correlation between the fluorine content of the frits or of the Na_2O or B_2O_3 contents was noted, which tends to disprove the theory that fluorine evolved from the enamels gives rise to nonsulfate scumming.

(2) Clays

Twenty-two clays from different shipments of foreign and domestic clays, both raw and refined, were tested. The effect of the drying temperature on the clays was studied. Eleven commercial enameling clays, including six domestic, one English, and four German Vallendar (raw Vallendar and Vallendar prepared by three different refining processes), were milled in amounts of 4, 6, and 8% in superopaque enamel A without an opacifier.

The twenty-two clays tested in the introductory survey test showed a variation over the entire scumming range from no scumming to complete covering of the test plate with scum. The same enamels milled with no clay did not scum.

Increased drying temperatures caused an increase in the scumming tendencies (see Table II).

TABLE II

EFFECT OF DRYING TEMPERATURE OF CLAYS ON SCUMMING

Drying temp. (°F.)	Scum (mm.)
Air dried	40
180	54
900	150

All of the clays in this test were milled according to the general mill formula (section II). Table III shows the results obtained with the eleven clays milled in various amounts with frit A without an opacifier.

TABLE III

EFFECT OF CLAYS ON SCUMMING

Clay No.	Type	Scumming (mm.) at 4%	6%	8%	Moisture (lb. H_2O/lb. dry air)
1	Domestic	None	None	None	0.0100
2	"	"	Trace	22	.0101
3	"	"	None	12	.0105
4	"	"	"	17	.0105
5	"	"	8	60	.0104
6	English	"	None	17	.0104
7	Domestic	"	Trace	10	.0098
8	Vallendar	"	"	24	.0099
9	"	"	"	20	.0105
10	"	"	10	50	.0099
11	"	"	Trace	15	.0098

When 8% of clay was added there was a wide variation in the amount of scumming; very little scumming when 6% was added; and no scumming when 4% was added. These data tend to show that the scumming tendencies of clays are markedly increased by increases in the percentage of clay and that clays used without opacifiers will cause scumming, although the amount of scumming is apparently increased by the opacifier.

(3) Opacifiers

Six commercial opacifiers were milled in frit A in amounts of 2, 4, and 6%, and Table IV shows the results of the test.

The effect of opacifiers on scumming seems to differ with various opacifiers. The amount of scumming in some cases was actually decreased, and with opacifier No. 6, it was entirely eliminated. In cases where scum-

ming accompanied the use of opacifiers, even though the addition of 2% of the opacifier decreased the scumming tendency of the enamel, this tendency was thereafter increased in every case by further additions of opacifier. The opacifier alone, however, is not responsible for scumming, but its use aggravates the scumming tendency which is caused by other mill additions.

TABLE IV

EFFECT OF OPACIFIERS ON SCUMMING

Opacifier No.	Scumming (mm.) at 0%	2%	4%	6%
1	35	40		60
2	35	45		70
3	35	10	14	18
4	35	6	35	55
5	35	Trace	Trace	Trace
6	35	None	None	None

Opacifier No. 2, 10%, no clay, no scumming
Moisture (lb. H_2O/lb. dry air), 0.0082 throughout.

(4) Electrolytes

The effect of nine electrolytes on scumming is shown in Table V.

TABLE V

EFFECT OF ELECTROLYTES ON SCUMMING

Electrolyte	Frit B (mm.)	Frit A (mm.)
Regular (check on humidity)		150
Sodium carbonate (1/8%)		150
Sodium nitrite (1/8%)		150
Boric acid (1/8%)		10
Hydrochloric acid (1 cc./250 cc. slip)		125
" " (5 " " " ")		30
" " (10 " " " ")		25
No electrolyte	20	27
Sodium nitrite (1/2%)	10	40
Sodium aluminate (1/2%)	15	50
Barium carbonate (1/8%) }	6	55
Barium chloride (1/8%) }		
Ammonium carbonate	20	None
Magnesium carbonate (1/4%)	85	60
Magnesium carbonate (1/2%)	20	35

The basic or neutral electrolytes, in most cases, either increase or have no effect on the scumming tendency. Ammonium carbonate, boric acid, and hydrochloric acid decrease scumming; 1/4% of magnesium carbonate increases scumming and 1/2% decreases it. The effect of the electrolytes on scumming apparently is correlated with their action on the clays.

(5) Drying Conditions

Sprayed enamels were dried at 180°F. and 300°F. in humid and dry atmospheres, but the drying temperature had little or no effect on the scumming condition.

(6) Spraying

Enamels were applied by wet and dry spraying. The wet spraying increased the scumming tendency; dry spraying decreased it; and a similar increase in scumming was noted when a freshly sprayed plate was tapped on a flat surface. The particle-size distribution and especially the final position of the fine frit and clay particles seem to be the governing factor in this case.

(7) Fineness of Grinding

In the preliminary survey, the enamels were milled to 1% on 325-mesh sieve, 1/2% on 200-mesh sieve, and 20% on 200-mesh sieve. The scumming tendency decreased with the fineness of grinding.

Frit A was then milled with Vallendar clay, using the opacifiers and finenesses in Table VI. The results are given in Table VII.

TABLE VI

Opacifier (%)	Fineness
None	1% on 325-mesh, 1/2 and 20% on 200-mesh
8 and 12% opacifier No. 3	5% on 200-mesh, 1% on 325-mesh
8 and 12% opacifier No. 4	"

TABLE VII

RELATION OF FINENESS OF GRINDING TO SCUMMING

Mesh fineness (%)	Opacifier	(%)	Scumming (mm.)	Moisture (lb. H_2O/ lb. dry air)
20 on 200	None	0	155	0.0110
1/2 on 200	"	0	35	.0110
1 on 325	"	0	Trace	.0110
5 on 200	No. 3	8	77	.0075
1 on 325	"	8	None	.0075
5 on 200	"	12		
1 on 325	"	12	82	.0075
5 on 200	No. 4	8	64	.0075
1 on 325	"	8	None	.0075
5 on 200	"	12	85	.0080
1 on 325	"	12	25	.0084

Although fine grinding greatly decreases the scumming tendency, the addition of high percentages of certain types of opacifiers was found to offset to a considerable degree the advantages gained through the fine grinding.

(8) Firing Treatment

The effect of differential firing on the scumming tendency of enamels has already been noted. The preliminary tests showed the humidity of the furnace atmosphere to exert a marked effect upon the scumming tendency, and high humidity atmospheres showed a much greater tendency to scum than the drier atmospheres.

Frit B, milled without opacifier but with 6% Vallendar clay, was tested daily for scumming over a period of three months. Fresh millings were used for each test. The temperature was held at 75°F. ±1°, and the extent of scumming was plotted against humidity (Fig. 1). These tests show that atmospheric humidity has a much greater influence in nonsulfate-type scumming than was previously believed.

Figure 1 shows that there is a mathematical relationship between relative humidity and scumming, i.e., that when the relative humidity rises above 33% at 75°F., the scumming tendency increases and the higher the humidity the more rapid the increase in scumming. Air with 33% relative humidity at 75°F. contains 0.0061 pound of moisture per pound of dry air.

Presuming that this amount of moisture is required to cause scumming, the higher the atmospheric temperature the lower the relative humidity that is required to cause scumming (see Fig. 2). Thus, if a 57% relative humidity causes scumming at 60°F., only 16% relative

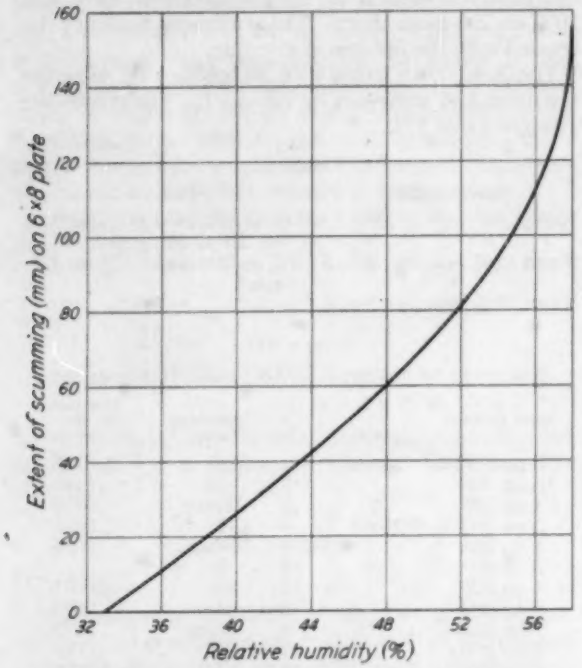

FIG. 1.—Relation of temperature to relative humidity to scumming; enamel B, no opacifier.

humidity is required at 100°F. In other words, the actual amount of water present in air varies with the temperature; e.g., there is more than twice as much at 100°F. with 33% relative humidity than at 75°F. with the same relative humidity. With a 33% relative humidity at 75°F., a 50°F. differential fire is required to cause scumming, but during the summer months when the temperatures and humidities are higher, less underfiring would be necessary.

(9) Cooling

The cooling treatment had no effect on the scumming of enamels.

IV. Comparison of Laboratory Results with Field Investigation

A study of the scumming data produced in the laboratory indicates that the firing, humidity of atmosphere, clays, opacifiers, and electrolytes are the major contributing causes of scumming. When these results were compared to actual plant investigations, an overloaded furnace chain and a differential temperature firing condition were encountered in practically every case of scumming. When the weather turned warm and humid, scumming began, and it disappeared when the humidity decreased. In one plant, humidity was correlated with scumming tendency quite accurately; e.g., scumming began during the last week in June, when three continuous days of high humidity were encountered, and it continued until about August 20, when it disappeared.

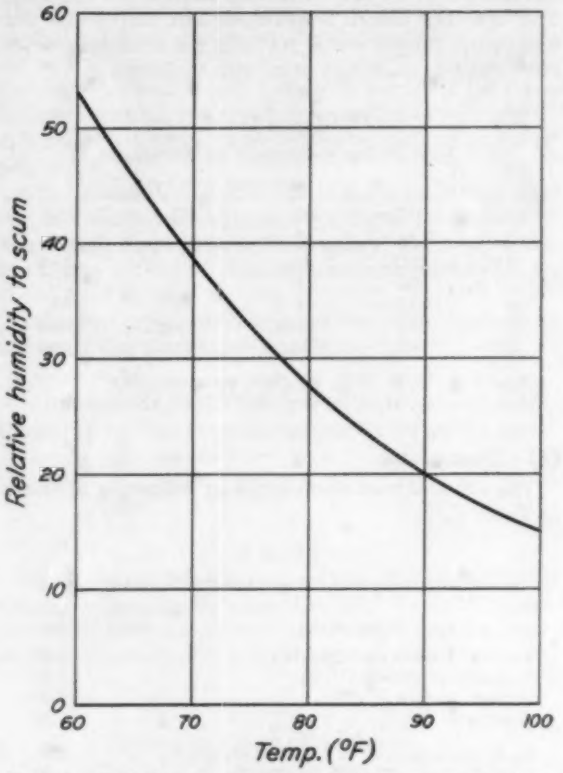

FIG. 2.—Relation of relative humidity to scumming; enamel B, no opacifier, temperature 75°F.

The moisture content as reported by the Weather Bureau during this time was as follows:

Month	Vapor pressure (mm. avg.)
Before June	<0.350
June	.457
July	.615
1st 19 days in August	.710
Following 6 days	.550

Where it was possible to compare different clays and opacifiers, their tendency to scum in the field agreed exactly with the laboratory findings. The laboratory results with electrolytes were also corroborated in the field.

V. Conclusions

Nonsulfate scumming seems to result from the combined effect of the types of frit, clays, opacifiers, firing conditions, fineness of grind, wetness of spray, electrolytes, and atmospheric humidity. Of these, differential firing, atmospheric humidity, and the types of clay and of the opacifiers used appear to be the major offenders. Of all the causes of scumming studied, clay was the only material or process, aside from highly exaggerated humidity, that would cause scumming unless one or the other factor was present.

It is indicated that nonsulfate scumming is caused by a reaction between clay and the moisture in the furnace atmosphere. Although the physical and chemical properties of the clay which cause this phenomenon have not been isolated, it would appear that particles of clay may remain suspended in the mill liquor rather than attach themselves to the frit particles and that they are carried to the surface of the enamel during the drying operation. The fluorine etching theory of scumming has not been substantiated. In plant practice, an overloaded furnace giving rise to differential heating or an improperly designed furnace in combination with high clay and high opacifier contents appear to be the major causes of this type of scumming.

PORCELAIN ENAMEL & MANUFACTURING COMPANY
BALTIMORE, MARYLAND

PHOSPHORUS STEELS FOR VITREOUS ENAMELING*

BY C. H. LORIG AND D. E. KRAUSE†

ABSTRACT

A summary is given of the tests which were conducted to appraise the utility of phosphorus steels in vitreous enameling. Enameling tests were conducted on both killed and rimmed steels of low-carbon iron and steel with a phosphorus content up to 0.60%. Phosphorus was found to reduce the sag of laboratory-prepared enameling stock to a marked degree. The most effective range of phosphorus was from 0.10 to 0.15%, and killed steels were superior to rimmed steels in their sag resistance. Phosphorus appeared to have no significant influence on common enameling defects. In amounts of less than 0.40%, it had no marked effect on the adherence of the enamel. The deep drawing qualities of the sheet, based on Olsen ductility tests, were somewhat impaired by phosphorus. This is in line with the strong tendency for phosphorus to raise the strength of the sheet.

I. Introduction

A summary is presented of tests which were conducted to appraise the utility of phosphorus steels in vitreous enameling.

Except for a recent patent,[1] nothing has been published on the use of phosphorus in enameling irons and steels. Although opinions differ as to ideal compositions of sheet for enameling, it is generally held that as far as chemical analysis is concerned the sheet should be low in carbon and in other metalloids. Sheets which are low in phosphorus have been the rule, the generally accepted maximum being 0.04%.

One characteristic effect of phosphorus that should be of value in enameling sheet is the increased hot strength and resistance to deformation at high temperatures that it confers to steel. Cross and Krause[2] reported the results of short- and long-time tension tests on a variety of low-carbon and low-alloyed steels with varying percentages of phosphorus. These writers clearly demonstrated that phosphorus raises the tensile and yield strength of low-carbon steel at temperatures of 750°, 850°, and 950°F. with little change in static ductility and that it produces increased resistance to deformation under sustained load at these same temperatures. A phosphorus content of about 0.10 to 0.35% was effective, and the high-temperature properties improved with increased phosphorus content. Speller[3] also reported an increase in the tensile strength of low-carbon steel at temperatures from 600° to 1000°F. when the phosphorus content was raised from 0.013 to 0.103%. The temperatures covered in the investigations mentioned were not as high as the maturing temperatures for vitreous enamels. It was reasoned that higher phosphorus in enameling iron and steel might effect improvements in strength at enamel maturing temperatures. Higher hot strength of enameling sheet should decrease the amount of sag during firing and should simplify to some extent the enameling process.

II. Experimental Work on Phosphorus-Bearing Enameling Iron and Steel

(1) Preparation of the Enameled Sheet

The sheets used in the enameling tests were prepared in the laboratory from heats of ingot iron, ferrophosphorus, and other minor additions that were cast into 13- or 14-lb. ingots. The ingots were hot-rolled,

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† Metallurgists, Battelle Memorial Institute, Columbus, Ohio.

[1] D. E. Krause (Monsanto Chemical Co.), "Vitreous Enameled Products," U. S. Pat. 2,109,271, February 22, 1938; *Ceram. Abs.*, **17** [5] 176 (1938).

[2] H. C. Cross and D. E. Krause, "Phosphorus as an Alloying Element in Steels for Use at Elevated Temperatures," *Metals & Alloys*, **8** [2] 53–58 (1937).

[3] F. N. Speller, "Discussion," *Proc. A.S.T.M.*, **24** [Part II] 162–64 (1924).

pickled, and cold-rolled to 20- or 22-gauge sheet, after which the sheets were either annealed or normalized. Enameling sheet of the type being considered is usually a rimming steel or low-carbon iron with a total metalloid content of not more than 0.15%. In this work, however, tests were run on both the killed and the rimmed steels and on the low-carbon iron with a phosphorus content up to 0.60%.

The cleaning, pickling, and rinsing of the sheet preparatory to enameling followed closely commercial practice. The enamels were milled from standard commercial sheet-iron frits to fineness values recommended by the suppliers. The weight of application varied somewhat between tests, but it was about $1^1/_4$ to $1^3/_4$ ounces per sq. ft. of sheet of dry enamel for the ground coat, which was applied by dipping on the two surfaces, and $1^1/_2$ ounces per sq. ft. of surface for each of the cover coats, the latter being applied by spraying only one surface of the sheet. The firing temperature during enameling varied with the type of enamel frit used, but it fell within the temperature range of 1500° to 1600°F.

Sag and adherence tests were made on the sheets and the surfaces were examined closely for defects.

(2) Physical Properties of Annealed Phosphorus-Bearing Sheet

Representative physical properties of annealed, enameling iron sheet containing phosphorus are listed in Table I. These irons were of the killed type and contained 0.01 to 0.03% C, 0.03 to 0.06% Mn, 0.02 to 0.07% Si, less than 0.03% S, and phosphorus as shown.

(3) Sag Tests

A preliminary test on the sag resistance of high phosphorus sheet was conducted at Battelle on 22-gauge annealed specimens, 4 by 10 inches in size, using an unsupported span of $8^1/_2$ inches. With a series of enameling irons, containing from 0.005 to 0.40% phosphorus, the measured permanent deflections or sag after firing were of the following order of magnitude:

Phosphorus content	Permanent deflection (inch)
0.005	0.10
0.110	0.00
0.210	0.02
0.400	+0.02 (arched upward)

The irons were enameled with a ground coat and two cover coats.

The Inland Steel Company conducted standard sag tests on three aluminum-killed irons (furnished by Battelle) containing 0.02 to 0.03% C, 0.03 to 0.05% Mn, 0.016% Si, under 0.03% S, and about 0.016% residual Al. The 22-gauge irons, which contained 0.16% P, were box-annealed for 5 hours at 1350°F. and were given a ground and a heavy cover coat of enamel. The amount of sag in this case was from 0.06 to 0.12 inch, whereas regular enameling stock of the same gauge gave a minimum of 0.30-inch sag. To compare their sag resistance further, a specimen of the high phosphorus iron and a specimen of the regular enameling stock were ground coated and fired at 1600°F. The former sagged 0.13 inch and the latter 0.39 inch. After applying a white cover coat and firing, the high phos-

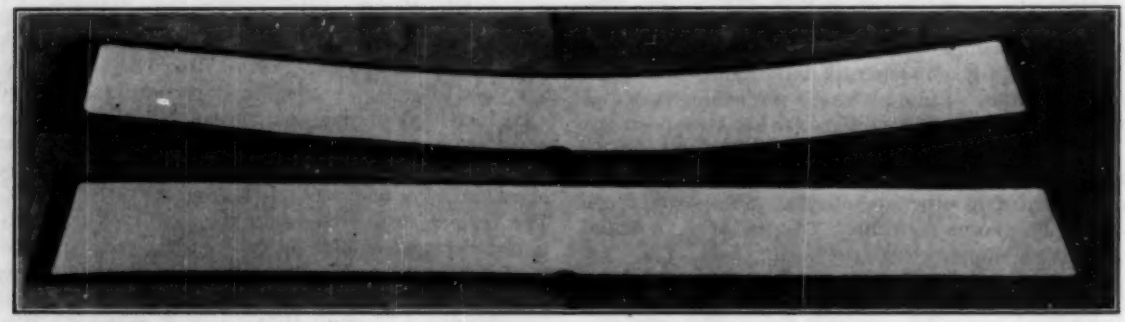

FIG. 1.—Comparative amounts of sag after enameling; regular enameling iron at top; experimental, high phosphorus iron (0.16% P) at bottom (approximately 0.6×).

TABLE I

REPRESENTATIVE PHYSICAL PROPERTIES OF ANNEALED PHOSPHORUS-BEARING ENAMELING IRON SHEET

Material	Phosphorus (%)	Strength: Tensile (lb./sq. in.)	Strength: Yield (lb./sq. in.)	Elongation in 2 inches (%)	Olsen ductility: Inch	Olsen ductility: Load (lb.)
Commercial	0.003				0.370	1500
"	.004				.290	1000
Experimental	.005	40,700	20,000	30	.290	1100
"	.11	46,900	24,400	27	.362	2000
"	.16	56,000	35,400	29	.368	
"	.21	55,000	37,200	31	.345	2400
"	.40	67,700	51,400	29	.328	2800
"	.60	73,800	57,100	23	.190	1500

TABLE II

SAG VALUES FOR RIMMED AND KILLED PHOSPHORUS-CONTAINING ENAMELING STEELS

Composition (%)					Box annealed (1300° F.)				Normalized (1800°F.) Box annealed (1300°F.)			
C	Mn	Si	S	P	Rockwell hardness "B"	Olsen ductility (inch)	Sheet gauge (inch)	Amount of sag (inch)	Rockwell hardness number	Olsen ductility (inch)	Sheet gauge (inch)	Amount of sag (inch)
					Rimmed steel							
0.06	0.015	0.003	0.027	0.007	45	0.375	0.0395	0.53	43	0.375	0.0385	0.58
.08	.017	.003	.029	.117	57	.347	.040	.33	53	.358	.0375	.48
.08	.013	.003	.032	.144	51	.334	.0375	.26	52	.362	.0395	.25
.08	.012	.003	.029	.157	63	.349	.039	.36	57	.359	.0375	.47
.08	.014	.003	.027	.180	63	.343	.0375	.32	59	.348	.0363	.69
.07	.013	.003	.029	.226	65	.349	.0395	.23	64	.302	.038	.37
					Killed steel							
0.06	0.042	0.003	0.029	0.008	50	0.355	0.039	0.33	40	0.400	0.037	0.27
.05	.052	.003	.027	.108	62	.367	.040	.17	61	.365	.038	.20
.04	.055	.004	.028	.134	63	.363	.0395	.23	58	.360	.0385	.18
.03	.058	.005	.028	.158	66	.366	.040	.21	64	.374	.038	.20
.08	.057	.004	.027	.181	68	.363	.040	.18	66	.339	.0375	.19
.08	.049	.005	.027	.208	71	.357	.040	.09	69	.353	.038	.17

phorus iron arched upward, showing a "negative sag" of 0.09 inch, whereas the regular enameling stock still showed a sag of 0.31 inch. Figure 1 shows the comparative amounts of sag.

On other standard sag tests run (by the Inland Steel Company) on killed and rimmed steels, prepared at Battelle, the phosphorus content of the steels covered a range up to 0.226%. The high carbon content of the heats, whose compositions are listed in Table II, would class all but two of them as enameling steel and not as enameling iron. The two exceptions are the heats listed under killed steels which contain 0.03 and 0.04% carbon. The fact that the majority of these materials are steels and not irons should be kept in mind, for example, when their sag resistance is compared with that of the three aluminum-killed irons mentioned before.

These steels were tested in the normalized, in the normalized and box-annealed, and in the box-annealed condition. The results of the sag tests on these materials, after box annealing at 1300°F. and after normalizing at 1800°F. and box annealing at 1300°F., have also been listed in Table II.

In these tests, the normalized and box-annealed samples of the killed steels with 0.10 to 0.20% P sagged far less than is usual for enameling iron, and they were satisfactorily uniform in behavior. The rimmed steels, on the other hand, varied considerably in sag resistance. Whereas the addition of phosphorus in the rimmed steels had the same general effect, though with a more variable response than it had in killed steels, a considerably higher phosphorus content apparently would be required to reduce the sag to that of the killed steel with only 0.10% P.

The test materials employed in these sag-resistance studies were prepared at Battelle. Several lots of phosphorus-bearing irons were processed under steel-plant production conditions, none of which duplicated the degree of improvement in sag that was obtained in the laboratory-produced irons. The underlying causes of this difference in behavior between the irons produced in the laboratory and those in the steelworks have not yet been determined.

(4) Adherence Tests

An impact test was employed to determine the relative adherence of enamel to flat sheets of varying phosphorus content. Little difference in adherence could be noticed until the phosphorus content was more than 0.4%. A 0.6% P iron showed poor adherence, but no difficulty was encountered in getting good adherence on flat sheets which contained up to 0.40% P.

III. Discussion

From an enameling standpoint, the high phosphorus materials enameled as well as regular enameling stock. The phosphorus content which is required to produce such beneficial results as have been described has not been found to promote any of the usual enamel defects, such as copperheading, blistering, reboiling, and fish-scaling. In fact, larger amounts of phosphorus than those mentioned here may be added and these benefits still be obtained, although the writers believe that the phosphorus content should be held below 0.40% in cases where enamel adherence is important.

The popularity of the enameling iron with low total metalloids is due to the uniformly high quality of the enamel coat or freedom from enamel defects, to its ability to withstand relatively severe drawing operations, and to its freedom from warpage or its warpage resistance as compared to steel. It is used in spite of certain shortcomings or limitations which this product is known to possess. For example, no element is present which confers strength at the firing temperature, and hence, only the resistance to sag of pure iron and that gained through special processing of the sheet is available.

Phosphorus appears to give the enameling iron and steel increased stiffness at high temperatures, and this was reflected in a marked reduction in sag during firing of the sheet made in the laboratory. The sag resistance at high temperatures increased with the phosphorus content, and the phosphorus appeared to be most effective in the range up to 0.1 to 0.15%. The results of the sag tests show that the treatment the material received is another important factor. Killed steels were markedly superior to rimmed steel not only in sag resistance

but in their uniformity of behavior. A box-annealing treatment, furthermore, gave better results than a normalizing treatment, though the difference in sag resistance between annealed and normalized stock was important only in the case of rimmed steels. The variation or uncertainty of sag resistance in the rimming steels which have been studied suggest a decided advantage for the killed type of iron or steel. This advantage of killed steel from a standpoint of sag resistance should not be construed as indicating that killed steel also excels as an enameling product. Experience has proved that this is not true. Sheets rolled from killed heats show considerably more enamel defects than those rolled from rimming heats, and many consumers of enameling sheet for this reason have standardized on rimming steel because of its better enameling quality.

At room temperature, phosphorus raises the strength of iron or steel; this was particularly reflected in the yield strength. As the enamel layer is not damaged by deformations below the yield point of the base metal, an increase in yield strength should mean more satisfactory ware.

Phosphorus has another important effect in raising the A_3 transformation temperature of iron at which a marked volume change occurs both on heating and cooling. This transformation takes place in enameling iron at about 1670°F., and to avoid the warpage that would be produced if this volume change were incurred in firing, frits are used whose maturing temperatures lie below 1670°F. Although a portion of the enameling industry uses enamels which may be fired at temperatures below that at which warpage occurs in the low-phosphorus enameling bases, an important branch of the industry is concerned with the use of the higher fusion enamels, which provide resistance to chemical attack and other advantages. Higher firing temperatures, which are permissible with the phosphorus-bearing irons and steels, will likely prove valuable for this purpose.

Various improvements may be expected from the addition of phosphorus. Enameling iron of the rimming type is red-short owing to its oxidized condition. Manganese may be added to eliminate some of the shortness and thus to improve the rolling of sheets, but 0.3% Mn lowers the A_3 point by about 75°F. Enameling iron, furthermore, has practically no strengthening elements, and if carbon, for example, is added, this element also lowers the A_3 transformation temperature. This transformation occurs with 0.15 to 0.20% C (with low P) at about 1540°F., but it is raised to 1595°F. by the addition of 0.1% P and to 1650°F. by 0.2% P. Thus phosphorus seems to give a wider firing range of irons or steels and greater latitude to the use of manganese and carbon for metallurgical or mechanical reasons.

Phosphorus-bearing enameling iron, in the present state of the art, is not subject to the degree of deep drawing as is that of standard enameling iron. Phosphorus increases the stiffness of the sheet, which makes some of the forming, drawing, and spinning operations more difficult. This characteristic influence would not be important for simple shapes and plain parts, but it may present problems when deep draws and stampings are required. There seems to be no reason, however, why the advantages of phosphorus additions cannot be realized for many applications, such as flat stock and simple shapes.

Earlier in this paper it was stated that mill development work on phosphorus-bearing enameling irons has been unable to substantiate some of the conclusions based on results actually obtained in the laboratory, particularly in relation to improved sag resistance. No commercially produced sheets therefore are available at this time. The beneficial influences obtained from the phosphorus irons and steels produced in the laboratory nevertheless should warrant the serious attention of the enameling industry. As a base metal for enamels with higher maturing temperatures, such as chemically resistant enamels, the phosphorus irons with their improved resistance to sag and a high transformation temperature should be useful.

IV. Summary

(1) Phosphorus reduces sag of laboratory-prepared enameling stock to a marked degree. It does not appear necessary to add more than 0.10 to 0.15% P, as larger amounts of phosphorus did not continue to reduce the sag to any extent. Killed steels were markedly superior to rimmed steels in their sag resistance and gave more uniform results.

(2) From an enameling standpoint, it appeared more desirable to gain strength in the sheet with phosphorus than with carbon.

(3) The A_3 transformation temperature of enameling iron is raised by phosphorus. The danger of warpage from phase changes during the enameling process may therefore be lessened by an increase in the phosphorus content of the sheet.

(4) As far as could be determined, phosphorus in enameling iron and steel does not promote or reduce the common enameling defects.

(5) In amounts of less than 0.40%, phosphorus in flat sheets appeared to have no marked effect on the adherence of enamel; the adherence was impaired by phosphorus contents above 0.40%.

(6) Drawing qualities of sheet are somewhat impaired by phosphorus, as shown by Olsen ductility tests.

Acknowledgment

The information presented herein was gained through research at Battelle Memorial Institute and the Inland Steel Company on the enameling of phosphorus steels. The authors also wish to express their appreciation to the Monsanto Chemical Company, which sponsored research at Battelle on phosphorus in enameling iron, and to the Inland Steel Company for information obtained in its enameling laboratory on steels made at Battelle.

Battelle Memorial Institute
Columbus, Ohio

AN INVESTIGATION OF THE VOLATILITY OF GLAZE CONSTITUENTS BY THE USE OF THE SPECTROGRAPH*

By H. C. Harrison, W. G. Lawrence, and D. J. Tucker†

Abstract

A procedure, developed for the study of volatile glaze constituents, consists of heating the glazes beneath an absorbing medium which is subsequently tested by the spectrograph for the volatilizable constituents evolved. Data are presented showing temperatures at which certain important glaze constituents begin to volatilize, the order in which they leave the parent glaze, the influence of glaze composition on the volatilization temperature of each volatilizable constituent, and the effect of heat treatment on the volatilization temperatures.

I. Introduction

Certain phases of glaze behavior were investigated, viz., (1) a qualitative study of some glazes to determine which of the constituents are volatile at chosen temperatures, (2) the ability of certain ceramic materials to function as an absorbent for these volatile constituents, (3) the lowest temperature at which a detectable amount of each constituent leaves the parent glaze, (4) the influence of glaze composition, and (5) the effect of heat treatment on the volatilization temperatures.

II. Test Apparatus

Figure 1 shows the equipment used in vaporizing and absorbing the glaze constituents. Because of the extreme sensitivity of spectrographic analysis, special care was taken to prevent contamination. The glaze specimen was placed in the bottom of the large crucible, which was 1 inch in diameter at the bottom, 2 inches at the top, and $2^1/_4$ inches high. The absorbing agent was contained in the smaller crucible, which was supported above the glaze by a clay triangle. The top of the larger crucible was covered with a loosely fitting lid made of the same material as the crucible. This apparatus was placed inside a silicon carbide muffle of a gas-fired furnace so that the glaze could be subjected to the heat treatment necessary to assure the absorption of the vapors for spectrographic analysis. The crucibles and covers were made of a vitreous whiteware body of the following composition: English ball clay 12.5, Kentucky ball clay 12.5, English china clay 17.5, Harris Lundy clay 7.5, flint 25.0, and Oxford feldspar 25.0%. The crucibles were fired to cone 11, and a spectrogram of the fired crucibles showed that they did not contain any of the volatilizable constituents studied.

A large Littrow model quartz spectrograph was used, and the arc method of spectral excitation was employed, using the direct current arc. Acheson graphite electrodes of low ash content, purified copper electrodes, and iron reference electrodes containing known impurities for use as additional references were employed. Eastman No. 33 and Eastman process spectrographic plates were selected for their contrast, fineness of grain, wide working range, and ease of handling in the dark room. The plates were developed with Rytol developer and were fixed in an acid-hardener fixing bath. The plates were dried and studied on the viewing stand and by the projection method.

III. Preliminary Tests

A preliminary investigation was necessary to determine the most suitable substance to be used as the absorbing medium. Various ceramic raw materials in powdered form, which were either neutral, acidic, basic, or amphoteric in chemical character, were used to collect the volatilizable constituents from a glaze containing tin, lead, boron, sodium, chromium, barium, and zinc and traces of arsenic and antimony as impurities. Eight crucibles were prepared, each containing three grams of the glaze, and a small crucible containing 0.5 gram of a different material as absorbing material. Later experiments indicated that 0.1 gram was the most efficient amount to use.

The crucibles containing the glaze and the absorbing medium were placed in a muffle furnace and heated to 1200°C. They were allowed to cool to room tem-

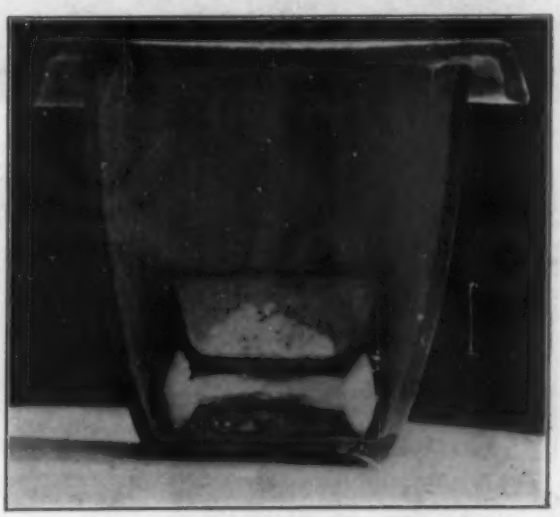

Fig. 1.—Crucibles used in glaze tests.

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† H. C. Harrison is Assistant Professor of Chemistry and W. G. Lawrence and D. J. Tucker are senior students at the New York State College of Ceramics, Alfred, N. Y.

perature, and the absorbing medium was removed, thoroughly mixed in an agate mortar, and 30-mg. portions were spectrographically analyzed. Spectrograms were taken of each of the electrodes, crucible, and the unfired absorbing medium. Table I shows the materials used as the absorbing media and the vaporized constituents absorbed by each.

Hydrated aluminum oxide and whiting are the most efficient absorbing media for the volatants studied, but the hydrated aluminum oxide was chosen for use in all of these experiments because it contains fewer impurities and gives a simpler spectrum than the whiting. None of the absorbing media was found to be alkali-free, so that a study of the alkalis was postponed to a later date. Figure 2 shows spectrograms of the aluminum oxide absorbing medium after certain of the volatile constituents of the glaze were absorbed.

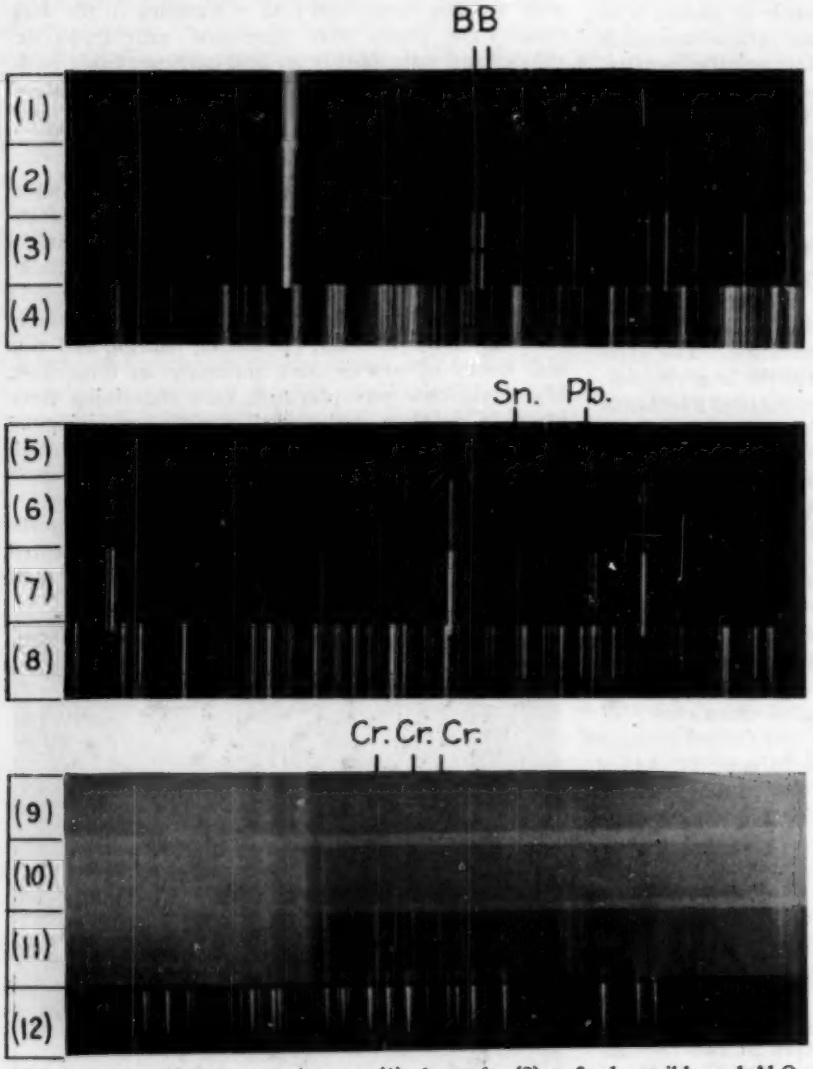


FIG. 2.—Absorbed element, boron: (1) electrode, (2) unfired crucible and Al_2O_3, (3) fired Al_2O_3, (4) iron; absorbed elements, Sn-Pb: (5) electrode, (6) unfired crucible and Al_2O_3, (7) fired Al_2O_3, (8) iron; and absorbed element, chromium: (9) electrode, (10) unfired crucible and Al_2O_3, (11) fired Al_2O_3, (12) iron.

IV. Volatilization Temperatures of Glaze Constituents

The investigation of the volatilization temperatures was limited to the elements, boron, lead, and chromium. (A separate study of the peculiar behavior of tin will be made later.) A cone 04 glaze was prepared as the source of the volatile constituents. The molecular formula is given in Table II. Five per cent tin oxide and 3% green chrome oxide were added to the batch of this glaze.

In the first experiment to determine the temperatures at which each volatile constituent started to leave the glaze, fourteen crucibles were used. Seven crucibles with 3 grams of glaze and 0.1 gram of hydrated aluminum oxide and seven crucibles with only 0.1 gram of hydrated aluminum oxide were slowly heated in the muffle furnace. Temperatures were determined with a Brown recording electrical thermocouple pyrometer and a platinum-platinum 10% rhodium thermocouple. The readings were checked with a Leeds and Northrup portable electrical thermocouple pyrometer.

One crucible containing the glaze and the absorbing medium and one without the glaze were withdrawn from the heated muffle at each 100°C. interval, starting at 600°C. and ending at 1300°C. The crucibles were allowed to cool to room temperature and spectrograms of the absorbing media were taken. The absorbing media from the crucibles with no glaze failed to show the presence of any of the volatile constituents. This indicates that the absorbing media had not been contaminated from any source. The results of this run are shown in Figs. 3, 4, and 5.

Figure 3 shows that boron appears strongly at 700°C. and decreases in intensity in the absorbing media heated to temperatures above 1100°C. Figure 4 shows lead appearing in the absorbing medium at 900°C., but not at 800°C. This places the temperature of volatilization of lead from this glaze somewhere between these two temperatures, assuming that the absorbing medium absorbs the volatile constituents as soon as volatilization starts. Lead appears strongly at 900°, 1000°,

TABLE I

Absorbing medium	Chemical character	Elements absorbed
English china clay	Nearly neutral	Pb, Cr, Sn, B
N. C. kaolin	" "	Pb, Cr, Sn, B
N. J. fire clay	Acidic	Pb, Cr, Sn, B
Flint	"	Pb, Sn, B
Flint fire clay	"	Pb, Cr, Sn, B
Hydrated aluminum oxide	Amphoteric	Pb, Cr, Sn, B, As, Sb
Fused magnesium oxide	Basic	B
Calcium carbonate (whiting)	"	Pb, Cr, Sn, B, As, Sb

TABLE II

0.40 PbO 0.25 CaO 0.25 KNaO 0.10 ZnO	0.28 Al_2O_3	2.75 SiO_2 0.375 B_2O_3

Batch composition	
White lead	10.32
Colemanite	51.5
No. 5 Minpro feldspar	152.3
Tin oxide	10.7
Green chrome oxide	11.2

and 1100°C., but only faintly at temperatures above 1100°C. Tin appears faintly at 700°C. and is strong whenever lead appears strongly. In every run made with a glaze containing both tin and lead, strong volatilization of lead is accompanied by strong volatilization of tin. The spectrogram showed the presence of chromium in the absorbing medium at 1100°C. but only faintly at 1000°C. It is impossible to reproduce in the spectrograms the faint chromium lines because of the dark cyanogen bands which are present in that portion of the spectrum. Sodium was present in the unheated absorbing medium as an impurity, but it appears only faintly in the absorbing media heated to temperatures above 1000°C. (Fig. 5).

To approximate more closely the temperature at which each volatile constituent starts to volatilize from the glaze, runs were made between the limits of 450° to 600°C., 800° to 850°C., and 950° to 1100°C., with draw trials taken every 25°C.

Figure 6 shows that boron is volatilized from this glaze at 450°C. and that its concentration in the absorbing medium increases with rise in temperature. Figure 7 shows the appearance of lead at 850°C. and of chromium at 1000°C.

V. Effect of Time on Volatilization Temperatures

Certain volatile constituents did not volatilize as readily when the muffle was heated rapidly as when it was heated slowly. This led to an investigation of the

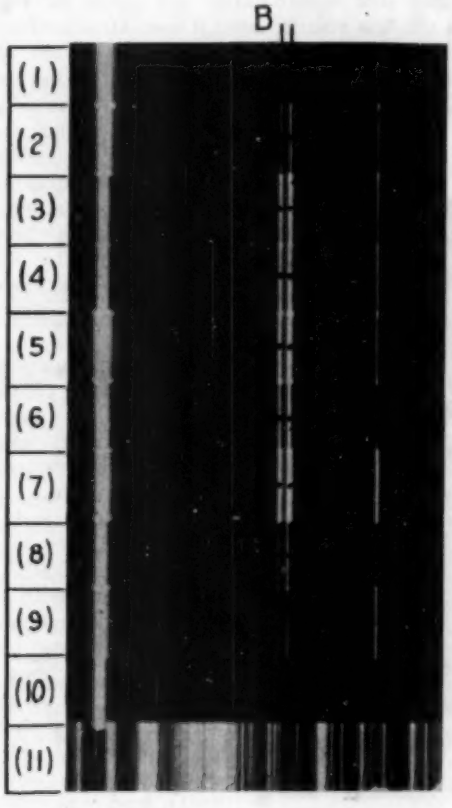


FIG. 3.—Absorbed element, boron: (1) electrode, (2) 600°C., (3) 700°C., (4) 800°C., (5) 900°C., (6) 1000°C., (7) 1100°C., (8) 1200°C., (9) 1300°C., (10) absorbing medium, (11) iron.

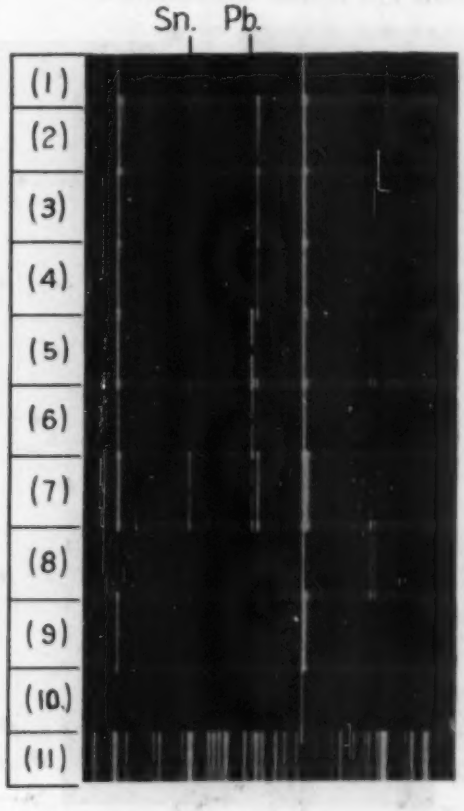


FIG. 4.—Absorbed elements, tin and lead: (1) electrode, (2) 600°C., (3) 700°C., (4) 800°C., (5) 900°C., (6) 1000°C., (7) 1100°C., (8) 1200°C., (9) 1300°C., (10) absorbing medium, (11) iron.

effect of soaking heat on the volatilization of the constituents of the glaze. This effect was more noticeable with chromium than with any of the other absorbing media.

Four crucibles were assembled, three containing the glaze and the absorbing medium and one containing only the absorbing medium. The crucibles were heated slowly in the muffle furnace, and when the temperature reached 450°C. one crucible was withdrawn; the muffle was then adjusted to maintain this temperature as closely as possible, and at the end of one hour another crucible was withdrawn. The heat was then shut off, and the remaining two crucibles, one containing the glaze and the absorbing medium and one containing the absorbing medium only, were allowed to cool to room temperature in the muffle. The absorbing media were then analyzed spectrographically. The same procedure was repeated at 850° and 1000°C.

The results of these runs indicate that the concentration of the volatile constitutents in the absorbing medium is increased by lengthening the period to which the glaze is subjected to heat. Sodium was present in appreciable quantities in the absorbing medium at 1300°C. when the muffle was heated rapidly, but when it was heated slowly, the sodium started to leave the absorbing medium at 1000°C., and it decreased in concentration with increase in temperature.

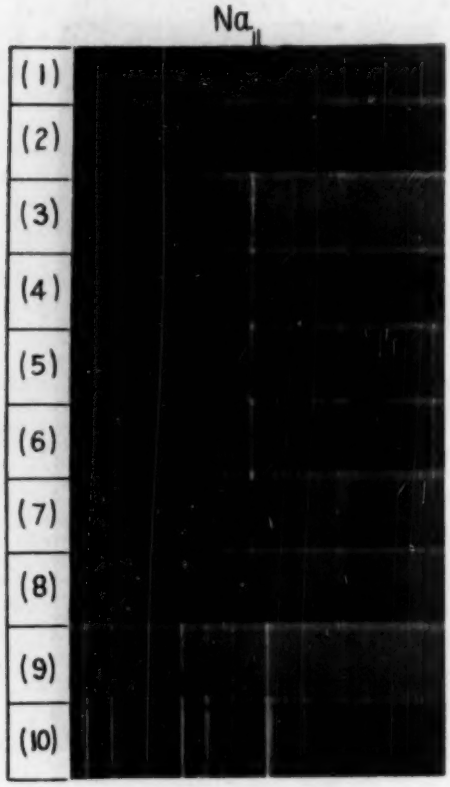


FIG. 5.—Absorbed element, sodium: (1) electrode, (2) 600°C., (3) 700°C., (4) 800°C., (5) 900°C., (6) 1000°C., (7) 1100°C., (8) 1200°C., (9) absorbing medium, (10) iron.

VI. Effect of Glaze Composition on Volatilization Temperature

The effect of varying the composition of the glaze on the temperature of volatilization was shown by use of a lead borosilicate glaze in which all of the boron and part of the lead were introduced in the frit and the remainder of the lead was added as white lead in the glaze batch.

TABLE III

$$\left.\begin{matrix}0.056\ KNaO\\ .446\ PbO\\ .500\ CaO\end{matrix}\right\}\ 0.27\ Al_2O_3\ \left\{\begin{matrix}2.7\ SiO_2\\ 0.32\ B_2O_3\end{matrix}\right.$$

Glaze batch (%)		Frit batch (%)	
Frit	36.8	Oxford feldspar	18.1
Whiting	7.4	Boric acid	24.0
White lead	15.5	Whiting	13.5
English china clay	15.0	Red lead	30.7
Flint	25.3	Flint	13.7

Ten crucibles were used, nine containing the glaze and the absorbing medium and one containing only the absorbing medium. Draws were taken every 100°C., from 500° through 1300°C.

The results of this test indicate that boron in a glaze of the composition given in Table III is slightly volatile at 500°C., with little change in volatility at higher temperatures (the spectrograms are given in Fig. 8). Boron was less volatile when it was introduced by fritting than as colemanite. Lead was present in the absorbing medium withdrawn at 800°C. but not at 700°C. The intensity of the lead lines decreased in the absorbing media heated above 1000°C. Although tin was not intentionally introduced in the glaze, its presence as an impurity was observed by its appearance in the absorbing medium after the heat treatment.

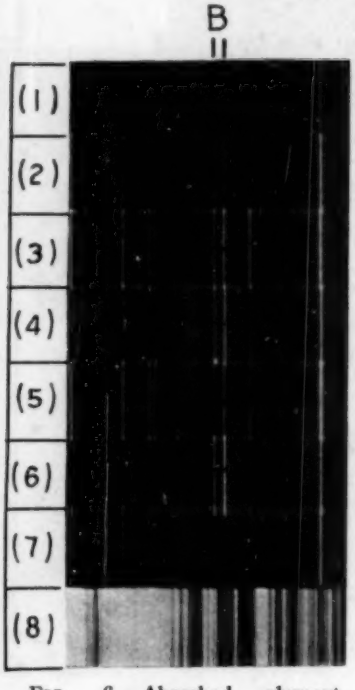


FIG. 6.—Absorbed element, boron: (1) electrode, (2) 450°C., (3) 500°C., (4) 525°C., (5) 550°C., (6) 600°C., (7) electrode and absorbing medium, (8) iron.

The silica content of the cone 04 glaze (Table II) was varied as shown in Table IV, and the effect on the volatilization temperatures was studied.

Glazes No. 1 and No. 2 were fired over a range from 500° to 1200°C. as in previous runs, with special attention to temperatures of 500°, 850°, and 1000°C.

The results show that boron is present in the absorbing medium at 500°C. in both cases. In glaze No. 1 (of lower silica content), lead was volatile at 800°C., and in glaze No. 2 (with a higher silica content) at 950°C. Chromium appeared in the absorbing

medium placed with glaze No. 1 at 1200°C., but it did not appear at 1200°C. in the glaze No. 2. This study indicates that the temperatures of volatilization of a glaze are influenced by the silica content of the glaze.

The results obtained by fritting a glaze or by varying the calcium or silica contents agree with the results obtained by Berdel,[1] who investigated the effect of the composition of the glaze on the volatility by a chemical analysis of the glaze before and after the heat treatment and by noting and analyzing the amount of glaze which collected on the covers of saggers.

TABLE IV

Glaze No. 1

$$\left.\begin{matrix}0.25\ KNaO\\ .25\ CaO\\ .40\ PbO\\ .10\ ZnO\end{matrix}\right\}\ 0.28\ Al_2O_3\ \left\{\begin{matrix}2.00\ SiO_2\\ 0.375\ B_2O_3\end{matrix}\right.$$

Glaze No. 2

$$\left.\begin{matrix}0.25\ KNaO\\ .25\ CaO\\ .40\ PbO\\ .10\ ZnO\end{matrix}\right\}\ 0.28\ Al_2O_3\ \left\{\begin{matrix}3.50\ SiO_2\\ 0.375\ B_2O_3\end{matrix}\right.$$

VII. Summary

A procedure is presented for studying certain phases of glaze behavior, in particular, the volatilization of glaze constituents. In this connection, the spectrograph has been a useful scientific tool.

Hydrated aluminum oxide was the most suitable collector or absorbing medium for this investigation.

The temperatures at which boron, lead, and chromium oxides start to volatilize from the cone 04 glaze studied were boron 450°, lead 850°, and chromium 1000°C.

The effect of soaking heat was found to give an increased concentration of the volatile constituents even after the muffle had started to cool.

An increase in the silica content of the cone 04 glaze increased the volatilization temperatures of boron, lead, and chromium oxides.

In the case of a high calcium glaze in which the B_2O_3 and part of the PbO were introduced in the fritted portion, the B_2O was less volatile at all tem-

[1] Edward Berdel, "Formation of Stalactites from Glazes in Tunnel Kilns," *Ber. deut. keram. Ges.*, **9** [1] 19–24 (1928); *Ceram. Abs.*, **7** [6] 394 (1928).

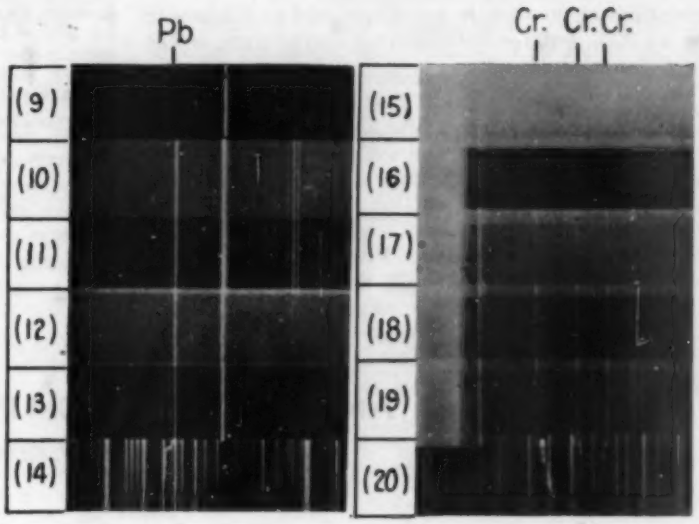


FIG. 7.—Absorbed element, lead: (9) electrode, (10) electrode and absorbing medium, (11) 800°C., (12) 825°C., (13) 850°C., (14) iron; absorbed element, chromium: (15) electrode, (16) electrode and absorbing medium, (17) 1000°C., (18) 1100°C., (19) soaking, 1100°C., (20) iron.

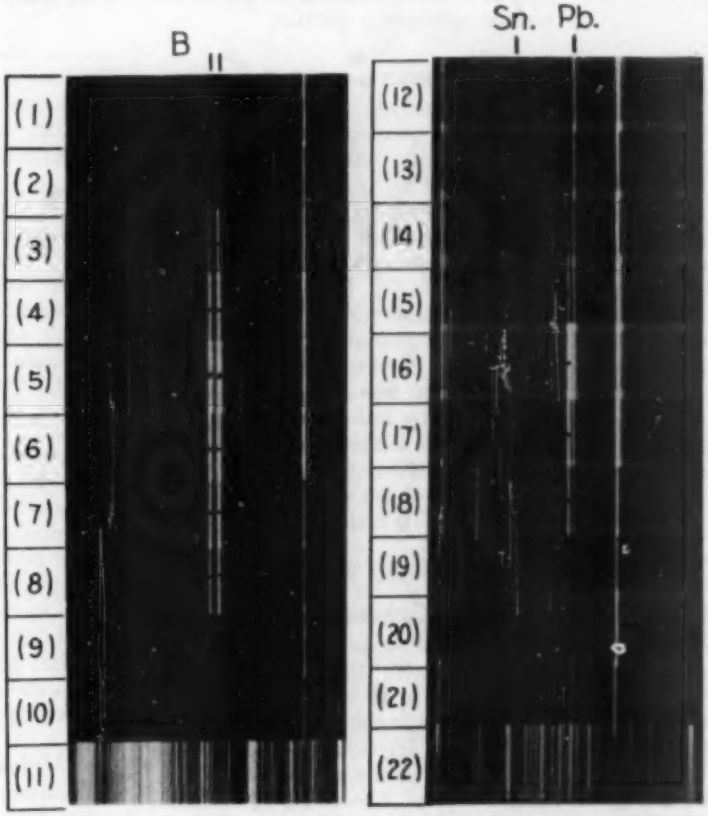


FIG. 8.—Absorbed element, boron: (1) 500°C., (2) 600°C., (3) 700°C., (4) 800°C., (5) 900°C., (6) 1000°C., (7) 1100°C., (8) 1200°C., (9) 1300°C., (10) electrode and absorbing medium, (11) iron; absorbed elements, tin and lead: (12) 500°C., (13) 600°C., (14) 700°C., (15) 800°C., (16) 900°C., (17) 1000°C., (18) 1100°C., (19) 1200°C., (20) 1300°C., (21) electrode and absorbing medium, (22) iron.

peratures than when it was introduced as colemanite or as B_2O_3, but the volatilization temperature of the PbO was lowered.

Acknowledgment

The authors wish to express their appreciation to M. E. Holmes, Dean of the New York State College of Ceramics, for advice and suggestions; to Leon B. Bassett for assistance in the procedure and the delineation of the spectrograms; and to other members of the faculty for their helpful suggestions and assistance.

New York State College of Ceramics
Alfred, New York

ANALYSIS OF SELENIUM IN GLASS*

By A. E. Pavlish and R. W. Silverthorn

Abstract

A new method for the determination of selenium in glass is reported. It comprises fusion of the sample with sodium carbonate, dissolution of the melt in sulfuric acid, distillation of the selenium as selenium tetrabromide from a sulfuric-hydrobromic acid solution, and titration of the distilled selenium by the iodide-thiosulfate method. The method is rapid, accurate, and precise and recovers all forms of selenium. The recommended procedure is outlined.

I. Introduction

The method[1] most commonly used to determine selenium in glass consists of decomposing the sample in hydrofluoric and nitric acids. After decomposition, the selenium is determined by a gravimetric, colorimetric, or volumetric procedure. The authors' experience with wet acid methods for decomposition of selenium glasses or compounds indicates that the results may be erratic.

Work was undertaken to develop a rapid and accurate method for the determination of selenium in glass. A method yielding excellent results and consisting of the following steps was developed, viz., (1) decomposition of the glass by fusion with sodium carbonate; (2) separation of the selenium from the sodium carbonate fusion by distillation from a H_2SO_4-HBr solution; and (3) titration of the selenium in the distillate by the iodide-thiosulfate method.

II. Experimental Work

(1) Fusion with Sodium Carbonate

Known amounts of selenium as CdSe, Se, $CdSeO_3$, and Na_2SeO_4 were fused with 10 grams of sodium carbonate for 15 minutes to ascertain whether any selenium was lost during the fusion. The selenium remaining in the fusion was determined by distillation and titration as described in the recommended procedure given in this paper. The forms of selenium added and the results obtained are shown in Table I. The recovery of various forms of selenium was quantitative in all cases. This is important in view of the fact that the selenium additions greatly exceeded the amount usually present in commercial selenium glasses.

(2) Separation of Selenium by Volatilization

Selenium may be separated quantitatively from a sulfuric acid solution by volatilization with hydrobromic acid.[2] Tetravalent selenium reacts with hydrobromic acid forming volatile selenium tetrabromide which may be separated by distillation. The distillation is rapid and no special equipment is required. The reaction may be expressed as

$$H_2SeO_3 + 4HBr \rightarrow SeBr_4 \uparrow + 3H_2O.$$

Metallic selenium or selenides are converted to selenites or selenates in the fusion step of the recommended procedure. Selenium present in the solution as selenate is reduced by hydrobromic acid to selenite.

The accuracy of the distillation procedure was determined by adding known amounts of selenium dissolved in sulfuric acid to the distilling flask which contained dilute sulfuric acid (1:1), hydrobromic acid, and bromine, and by determining the selenium in the distillate. The results given in Table II show that the recovery of selenium by distillation was excellent.

(3) Volumetric Determination of Selenium in the Distillate

Selenium may be determined quantitatively in acid solution by reduction with potassium iodide and titra-

* Received January 2, 1940.

[1] N. H. Furman, Editor, Scott's Standard Methods of Chemical Analysis, Vol. I, p. 791. D. Van Nostrand Co., Inc., New York, N. Y., 1939.

[2] J. I. Hoffman and G. E. F. Lundell, "Volatilization of Metallic Compounds from Solutions in Perchloric or Sulfuric Acid," *Jour. Research Nat. Bur. Stand.*, 22, 465–70 (1939); R.P. 1198.

tion of the liberated iodine with a standard sodium thiosulfate solution. The following reactions are involved in the titration:

$$SeBr_4 + 3H_2O \longrightarrow H_2SeO_3 + 4HBr$$
$$H_2SeO_3 + 4KI + 2H_2SO_4 \longrightarrow Se + 2I_2 + 2K_2SO_4 + 3H_2O$$
$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI.$$

The selenium volatilized during the distillation may be recovered by catching the distillate in approximately 200 ml. of a 1% sulfuric acid solution which contains 1 ml. of hydrobromic acid and 1 ml. of bromine water. Work by the writers indicated that either sulfuric or nitric acid may be used in the receiver, but the former is preferable. The concentration of free acid in the receiver has little or no effect on the recovery of selenium during distillation, but too high a concentration of free acid will affect the accuracy of the titration. A concentration of 1% of sulfuric acid, by volume, is the most satisfactory. The addition of bromine and hydrobromic acid to the receiver is advisable to insure conversion of the selenium to selenite. After the distillation is complete, free bromine which interferes with the subsequent titration is reduced by the addition of formic acid.

TABLE I

EFFECT OF Na_2CO_3 FUSION ON RECOVERY OF VARIOUS FORMS OF SELENIUM

Selenium added as	Selenium (gm.) Present	Found	Difference
Metallic selenium	0.0100	0.0101	+0.0001
	0.0100	0.0100	0.0000
Cadmium selenide	0.0074	0.0073	−0.0001
	0.0074	0.0074	0.0000
Cadmium selenite	0.0060	0.0059	−0.0001
	0.0060	0.0062	+0.0002
Sodium selenate	0.0082	0.0082	0.0000
	0.0082	0.0082	0.0000

TABLE II

RECOVERY OF SELENIUM FROM SYNTHETIC SAMPLES

Synthetic sample	Selenium (gm.) Present	Found	Difference
1	0.0002	0.0002	0.0000
	0.0002	0.0002	0.0000
2	0.0006	0.0006	0.0000
	0.0006	0.0006	0.0000
3	0.0016	0.0016	0.0000
	0.0016	0.0017	+0.0001
4	0.0020	0.0020	0.0000
	0.0020	0.0020	0.0000
5	0.0030	0.0029	−0.0001
	0.0030	0.0029	−0.0001

The concentration of sulfuric acid in the receiver is not critical so far as absorption is concerned, but high concentrations lead to erratic results in the titration when arsenic is present in the glass. Selenium ruby glasses occasionally contain arsenic, at least a portion of which is volatilized during the distillation. When arsenic is present, the end point may return faster than when it is absent, but when the recommended procedure is followed this effect is minimized and the accuracy of the method is not impaired.

(1940)

III. Recommended Procedure

Transfer a 1-gram sample to a 50-ml. platinum crucible containing approximately 6 grams of sodium carbonate. Mix the sample and sodium carbonate thoroughly with a glass rod, add a layer of 4 grams of sodium carbonate, and fuse the contents of the crucible over a Fisher or Méker burner for 10 to 15 minutes. Melt the sides of the crucible clean before removing from the burner and cool the crucible and its contents to room temperature. Remove the fusion by rolling the crucible lightly in the palms of the hands. Break the fusion into small pieces and transfer to the distilling flask, *A*, shown in Fig. 1. Add hot dilute H_2SO_4 (1:1) to the empty platinum crucible and heat the crucible and its contents until complete dissolution of the fusion adhering to the sides of the crucible is

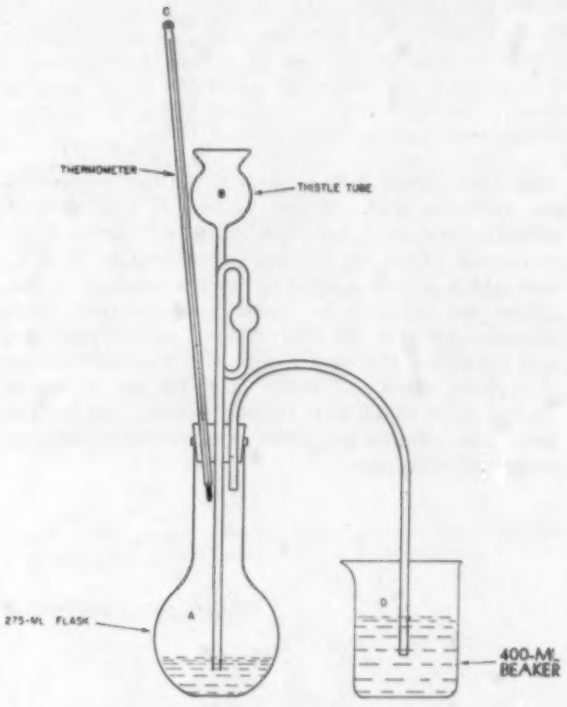


FIG. 1.—Distillation apparatus.

effected. Transfer the H_2SO_4 from the crucible into the distilling flask and then add enough dilute H_2SO_4 (1:1) to make the volume in the distilling flask approximately 40 to 50 ml. Add a few small pieces of porous plate to the distillation flask to prevent bumping during the distillation. Prepare the receiving solution by adding to a 400-ml. beaker 175 ml. of dilute sulfuric acid (1:99), 1 ml. hydrobromic acid, and 1 ml. bromine water. Add 5 ml. hydrobromic acid and 1 ml. bromine water to the distilling flask, stopper it, and proceed with the distillation. Start the distillation by heating with a low flame to allow the fused mass to disintegrate. During the distillation, the temperature of the distilling vapor gradually rises approximately to 123°C.; it remains at this point until the hydrobromic acid and

selenium have distilled over and then drops several degrees. When the drop in the temperature occurs, the distillation of selenium is complete. Disconnect the apparatus and wash the delivery tube with distilled water, adding the washings to the receiving solution.

TABLE III

ANALYSIS OF VARIOUS SELENIUM GLASSES BY RECOMMENDED PROCEDURE

Glass sample	Selenium (%)
1	0.015
	0.015
2	0.018
	0.019
3	0.034
	0.034
4	0.050
	0.051
5	0.078
	0.078
6	0.099
	0.100
7	0.108
	0.108
8	0.148
	0.145

Add 5 ml. formic acid to destroy the free bromine in the receiving acid. If the solution is not perfectly colorless, heat on a hot plate until the bromine is decomposed. Cool the solution approximately to 20°C. and add 6 ml. of a 50% by weight solution of KI. Allow the solution to stand approximately three minutes, add the freshly prepared starch indicator, and titrate the liberated iodine with standard sodium thiosulfate solution at a rate of 10 ml. per minute to an end point which lasts for one minute. At the end point, the solution has a yellow or red color owing to elemental selenium.

1 ml. 0.005 *N* $Na_2S_2O_3$ = approx. 0.0001 gm. selenium.

Reagents Used for Selenium Glass Determination

Sodium carbonate, C.P. anhydrous.
Sulfuric acid solutions, 1–1 by volume and 1% by volume.
Bromine water, distilled water saturated with bromine
Hydrobromic acid, 48% C.P.
Formic acid, 87% C.P.
Standard sodium thiosulfate solution, approx. 0.005 *N*.
Potassium iodide solution, 50% KI, C. P., by weight.
Soluble starch solution, 5 gm. soluble starch per liter.

IV. Discussion

Several hundred determinations of selenium in glasses of various base compositions have been made by the procedure outlined in this paper. Table III shows typical results obtained by the method. The method has proved to be an excellent one, inasmuch as it is rapid and requires no special equipment or skilled manipulation. A single determination of selenium in glass may be made in 30 minutes, whereas methods previously reported require several hours for completion.

The determination of selenium in glass by acid methods of decomposition is open to question because certain forms of selenium may be lost by volatilization. These methods are also slow and require careful control of the temperature to minimize the danger of loss of selenium. Experimental work reported in this paper shows that no form of selenium likely to occur in a selenium ruby glass is lost by fusion with sodium carbonate. The method has an accuracy and precision of ±0.001% selenium on ordinary selenium-bearing commercial glasses.

BATTELLE MEMORIAL INSTITUTE
COLUMBUS, OHIO

STRESSES IN BOTTLES OR JARS FROM DIFFERENCES IN OUTSIDE AND INSIDE TEMPERATURES (STATIC TEMPERATURE GRADIENT)*

By F. W. Preston

Abstract

This investigation shows that there is likely to be a severe concentration of stress in bottles or jars on the outside face of the junction of side walls and base when the bottles are subjected to a thermal gradient, that is, hot inside and cold outside. The stress in this area apparently may be two or three times as high as the general average, and its amount depends on the details of design at this point. A general formula, intended as a first approximation to the stress, has been worked out. That this region is a region of weakness is not news, but the reasons for it, as deduced in this study, are different from those generally given. Murgatroyd has shown that scratches on a bottle have a greater influence here than elsewhere and that their vulnerability is greatest if they are horizontal. His results are empirical, and he does not explain them. The explanation is given here.

I. Introduction

Bottles, in general, are not subjected in practice to steady temperature gradients for very long, and this investigation was conducted because it is amenable both to mathematical and experimental investigation. In the pasteurizing process, some bottles are subjected to a long-enduring temperature gradient, but its actual value in many cases is probably rather low. On the other hand, there are various occasions when a severe gradient, not strictly long-enduring but of a duration sufficient to cause trouble, occurs in practice. A bottle of "soda," for example, taken from a warm room and put in an ice box or possibly in a tank of ice-water, is subjected for some moments to a severe temperature gradient, or a Mason jar, initially at little above room temperature, may be poured full of boiling fruit juices. The stress conditions in either case pass through an elaborate cycle, but at their worst, momentarily or for a longer time, they approximate to static conditions.

II. Experimental Methods

The temperature of the outside wall of a glass vessel which is filled with hot water may differ a great deal from the temperature of the air of the room, and some parts of the outside of the bottle may also vary in temperature from other parts. It becomes necessary, therefore, to simplify this problem by specifying that the temperature of the outside of the bottle be maintained substantially constant, both in time and over the whole surface, by immersing it in a circulating fluid, such as water of constant temperature.

In the experimental arrangements, water or carbon tetrachloride (for better matching of refractive index) is circulated inside the bottle, and a similar fluid is circulated outside in an "aquarium" or immersion bath.

(1) Stresses in Side Walls

As far as breakage is concerned, the base and lower part of the side walls are of interest; only occasionally does breakage occur elsewhere. The junction of the base and side often appears to be the most vulnerable region.

The expansion is studied on an infinitely long cylinder with hot water inside and cold water outside at temperatures, θ_1 and θ_2, respectively, which are also assumed to be the temperatures of the surfaces of the glass. If this be inadmissible, it may be corrected later, but for comparing the base and sides and the junction of the two, it will be assumed for the present. (R equals the internal radius of the cylinder at the zero of the particular temperature scale ($\theta = 0$), and t equals wall thickness, which is small compared with R). Under a steady régime, then, the temperature gradient is uniform through the wall thickness, $(\theta_1 - \theta_2)/t$, which is termed $\bar{\theta}/t$ (see Fig. 1). The cylinder will expand both in length and in diameter, but it will remain a cylinder and the plane cross sections will remain plane. If α be the coefficient of expansion, then R will expand to

$$R\left(1 + \alpha\frac{\theta_1 + \theta_2}{2}\right).*$$

* This is true to the first order of small quantities and depends on the postulate that t is small compared with R.

Similarly, t expands to

$$t\left(1 + \alpha\frac{\theta_1 + \theta_2}{2}\right) \qquad (1)$$

and parallel to the axis, and the cylinder expands in like ratio.

The cylinder could expand in all directions and be free from stress if the glass were all at one temperature, but a difference of temperature between the different parts is assumed and stresses may or may not be developed. In the case of the cylinder, stress is developed because the periphery of the cylinder is complete. If the cylinder were split parallel to the axis, the split would open slightly under the temperature gradient, and the horizontal (peripheral) tension would disappear; in practice, bottles often do split in this fashion.

Halfway through the wall thickness of the cylinders, there is no stress; outside of this area, a tension occurs whose intensity increases toward the outer surfaces and a compression occurs inside whose intensity increases toward the inner face.

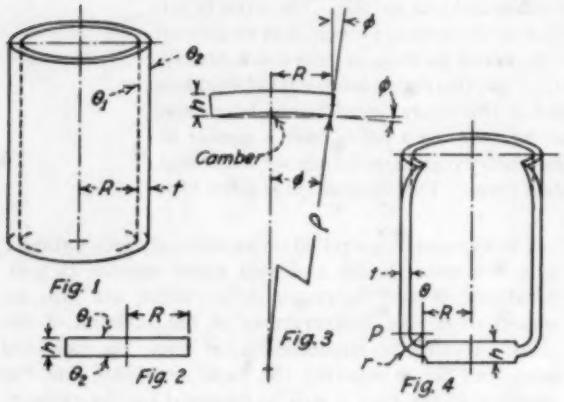
* Received November 13, 1939.

At the outer face, the uncompensated (or unachieved) expansion per unit of length is

$$\alpha\left(-\theta_2 + \frac{\theta_1+\theta_2}{2}\right) = \alpha(\theta_1-\theta_2)/2 = \alpha\bar{\theta}/2. \quad (2)$$

The resulting stress is

$$E\alpha\bar{\theta}/2. \quad (3)$$



FIGS. 1–4.

(2) Stress in Base

The base of a bottle is regarded as a flat circular plate with parallel faces. The dimensions and assumed temperature conditions are given in Fig. 2. The upper face expands until its radius, R, becomes $R(1+\alpha\theta_1)$, and the lower face expands to $R(1+\alpha\theta_2)$; the difference is $R\alpha\bar{\theta}$. If there are no constraints, i.e., if the base is connected in an exceedingly flexible manner with the sides, then the base, instead of being a flat plate, becomes a segment or cap of a sphere (Fig. 3). Let ρ be the radius of this sphere; then the angle φ, being small, is given (in radians) by R/ρ, or $R\alpha\bar{\theta}/h$.

Therefore,

$$\rho = h/\alpha\bar{\theta}. \quad (4)$$

If $h = 1/4$ in., $\alpha = 50\times10^{-7}$/°F., and $\bar{\theta} = 100$°F., then

$$\rho = \frac{10^7}{200\cdot100} = 500 \text{ inches}.$$

The amount of "crowning" or "camber" introduced in the base is

$$R^2/2\rho. \quad (5)$$

If $R = 1$ inch (the bottle being about 2 inches inside diameter), then the amount of camber is 0.001 inch, and the bottle base becomes dimpled to this extent (Fig. 3).

The slope, ϕ, at the margin of the base is given by

$$\phi = R/\rho \text{ (radians)}. \quad (6)$$

For example, in the case under discussion, $\phi = 1/500$ radians = approx. 1/9 degree.

These changes of length and shape involve no stresses in the glass because they are not resisted, but each element or filament of glass is free to adopt the length appropriate to its temperature.

The base, in practice, is always attached more or less firmly to the sides, and the postulated absence of constraint is not realized. The base is strained by the rigidity of its connection to the side walls, and this connection is strained by the rigidity of the base.

(3) Stress in Base and Side Walls

The connection between the base and side walls is assumed to be a web of glass equal in thickness to the side walls, t, with a radius in vertical section of r, wherein r is small compared with R (Fig. 4). The base is so rigid that it insists on taking the camber previously calculated and the slope at the edge, given by angle ϕ; the sides above point P are very rigid and take the dimensions indicated by equation (1) and retain their strictly cylindrical shape. These assumptions are only half true (or a little more than half true) and insofar as they are untrue, the following calculated stresses for the connection are diminished in practice.

The arc, PQ = 90 degrees in the unstrained condition = $\pi/2$ radians.

In the strained condition, the arc becomes

$$\left(\frac{\pi}{2} + \phi\right) \quad (7)$$

The radius, r, decreases to r_1, where

$$r_1\left(\frac{\pi}{2}+\phi\right) = r\cdot\frac{\pi}{2}. \quad (8)$$

The elastic strain is readily deduced to be

$$\phi\cdot t/\pi r. \quad (9)$$

In the case under consideration, $\phi = 0.002$. Then if $t = 1/8$ inch and $r = 1/4$ inch, the strain $= \frac{0.002}{2\pi} = 32\times10^{-5}$.

The tension developed is

$$E\phi t/\pi r. \quad (10)$$

Then if E is 10^7 lb. per sq. in. in this case, the tension would be 3200 lb. per sq. in.

To this must be added the stress due to the temperature gradient itself, viz.,

$$E\alpha\bar{\theta}/2 \text{ (see equation (2))}. \quad (11)$$

This addition amounts to 2500 lb. per sq. in., and the combination of the two is 5700 lb. per sq. in., which is probably all the bottle can stand.

In equation (10), if the value of ϕ, as defined by equations (6) and (4), is substituted for ϕ, then

$$\text{Tension } f_b = ERt\alpha\bar{\theta}/\pi rh \text{ (stress from flexing)}. \quad (12)$$

The direct thermal stress is

$$f_t = \frac{E\alpha\bar{\theta}}{2},$$

and the total stress is

$$f = f_b + f_t = E\alpha\bar{\theta}\left[\frac{Rt}{\pi rh} + \frac{1}{2}\right]. \quad (13)$$

In practice, this probably represents an outside value, and the true figure is somewhat less, but it is sufficiently

high that glass can endure it only for a few seconds at most if its surface is in any way bruised, scratched, or imperfect.

For example, in a room at 70°F., a half-gallon Mason jar is half filled with boiling water (at about 210°F.). For the constants of equation (13), values are as follows:

$E = 10^7$ lb./sq. in.; $\alpha = 50 \times 10^{-7}$/°F.; $\tilde{\theta} = (210 - 70) = 140$°F.

$R = 2$ in.; $t = 1/8$ in.; $r = 1/4$ in.; $h = 1/4$ in.; and $\pi = 3.14$.

Then $f = 7000\left[\frac{1}{\pi/4} + \frac{1}{2}\right] = 12{,}000$ lb./sq. in.

Therefore the glass must be expected to break.

If the bottle stands in air and not in a tray of water, $\tilde{\theta}$ never reaches 140° differential because the outside of the jar warms up to a temperature which is greater than the room temperature. But if the jar stands in cold water, it will break every time, in spite of the fact that the static conditions postulated are never quite attained and that all of the various ameliorating circumstances mentioned operate to reduce the calculated stress in practice.

III. Experimental Verification

The formula of equation (13), viz.,

$$f = E\alpha\tilde{\theta}\left[\frac{Rt}{\pi rh} + \frac{1}{2}\right],$$

makes it apparent that no correlation will exist between the weight-to-capacity ratio and the thermal-shock strength. The formula suggests, however, that there will be a strong negative correlation between the thermal-shock strength and

$$\left(\frac{Rt}{\pi rh} + \frac{1}{2}\right)$$

(the correlation, of course, will not be linear).

$$\text{If } \left(\frac{Rt}{\pi rh} + \frac{1}{2}\right) = J, \text{ then } \tilde{\theta} \cdot J = f/E\alpha. \qquad (14)$$

This is true in any particular breakage, and it may be easily shown that this is also true for averages.

Therefore,

$$\text{Average } \tilde{\theta} \cdot J = \frac{\text{avg. stress}}{\alpha E} \text{ or average } \tilde{\theta} \cdot J = \text{constant.}$$

This idea has been used for tests on some bottles, greatly differing in size, made from glass in the same tank and on the same type of machine. Table I gives the data and calculations.

The results seem a trifle too good to be true, but they tend to bear out the theoretical work; it might even seem wiser to go to the added expense of following along this line of thought rather than the apparently more barren field of the effect of weight-to-capacity ratio on thermal-shock strength.

Several varieties of bottles have been observed, and it was noticed that the variations in these dimensions would account for the differences in the thermal-shock strength of the bottles, which hitherto were blamed more or less on "flaws" in the bottles.

The chief difficulty of measurement lies in the variability of the dimensions of the bottles and also in the fact that the assumptions made in the configuration of the theoretical bottle are not closely met. Somewhat arbitrary points of measurement, therefore, were necessary. The base was measured half way between the center and the outside, and the curvature was considered in the region in which the fracture usually starts. The thickness of the side wall was measured at the rim at an angle of 45 degrees with the side wall.

TABLE I

Type	Thermal shock strength	R	T	h	r	J	$\tilde{\theta}J$
"7 UP"							
6 oz.	98	0.87	0.37	0.24	0.25	2.20	216
12 oz.	88	1.10	0.32	0.24	0.25	2.40	212
24 oz.	82	1.50	0.43	0.33	0.30	2.60	213
32 cap.							
28 oz.	85	1.50	0.35	0.33	0.25	2.50	213

Even with these limitations, an error of 5% may easily be made in the measurements, indicating the necessity of improving the technique of measurement in order to go further with the problem.

Warning: Table I shows that the thermal-shock strength, $\tilde{\theta}$, does not vary over a very wide range and that $(J - 1/2)$, which is a description of the geometry of the bottle, therefore varies only over the range 1.7 to 2.1. This range is not wide enough for conclusive proof, even though the individual elements which make up the geometry have appreciably greater variations.

A more elaborate investigation showed that the thermal-shock level to be expected could not be defined solely in geometrical terms. Five factors, always involved in the thermal-shock strength of glass, are essentially as follows: (1) degree of temper of the bottle; in one investigation, variations of temper caused the strength of the bottles to vary from 104° to 117°F.; (2) degree of cordiness of the bottle; (3) local irregularities in the glass caused by cut-offs, shear marks, baffle marks, etc.; (4) degree of bruising a bottle has had; and (5) geometry of the bottle, which is the only factor that can be taken into account in the present memorandum.

IV. Practical Application

This investigation, begun three years ago, shows the tendency to stress concentration in this region; the recommended procedure has been a tapering in of the lower side wall of the bottle so that there is less danger of the bottles getting scratched or bruised in the "Murgatroyd belt." It also aids in getting good glass distribution and hence is favored in the manufacturing shops.[1]

[1] L. G. Ghering, "Improving the Strength of Glass Containers Through Design," *Glass Ind.*, **20** [12] 443–47, 472 (1939).

PRESTON LABORATORIES
BUTLER, PENNSYLVANIA

EXPANSION STRAINS IN THE INITIAL FIRING OF CERAMIC WARE*

By G. E. Sievert and J. Moffat, Jr.

Abstract

The initial firing of some ceramic bodies is accompanied by a preliminary expansion before shrinkage takes place. This expansion, which has been determined for several types of ceramic bodies, may set up strains and result in the cracking of large pieces when they are improperly fired. A firing schedule that will lessen the strains and eliminate the cracking has been effected and is described in this paper.

I. Introduction

A shrinkage normally occurs when green clay products are fired. Some products, however, expand in the first part of the firing period before shrinkage begins, often causing strains and thereby defective products. Instances have been known of defects in ware caused by improper firing procedure which have been incorrectly attributed to too rapid water-smoking or to other causes. In many instances, however, the defects were caused by strains due to expansion and shrinkage of the ware during an improper firing schedule.

II. General Behavior of Unfired Ware in Initial Heat Treatment

Figure 1† shows the expansion and shrinkage behavior of some ceramic bodies upon being heated the first time. Curve (1) is a silica brick; (2) a dry-pressed clay firebrick; (3) a special type of vitreous china body; (4) a standard type of vitreous china body prepared from feldspar, silica, and clays; and (5) a wall-tile body. All of these bodies showed the same expansion characteristics before shrinkage when they were heated the first time. This expansion, in many cases, is greater than that of the same body when it is reheated after being fired. There is also a wide variation in the behavior of the different bodies at the peak of the expansion. Some bodies begin to shrink immediately after the expansion stops, while others have a fairly wide temperature range in which there is little change in volume.

This characteristic of ceramic bodies does not normally cause defective ware when it is fired on average schedules because of the relatively small size of the pieces. If, however, large pieces of ware are to be fabricated from these bodies, the firing schedule must be such that it will allow for expansion behavior. It is possible that some of the cracking of the larger pieces, such as large vitreous china lavatories, stall urinals, and large sewer pipe may be caused by their expansion during firing.

III. Outline of the Specific Problem

Excessive losses in large fireclay blocks for glass-melting furnaces occurred following a change in the composition of the body. The new body had a greatly reduced volume porosity as compared with the former one. (The pieces were solid blocks, 12 inches thick, 18 to 24 inches wide, and 36 to 54 inches long.) When blocks of the original mix were fired on standard schedule, they developed less than 2% loss in firing, but the new mix on this same schedule resulted in a kiln loss of approximately 100%.

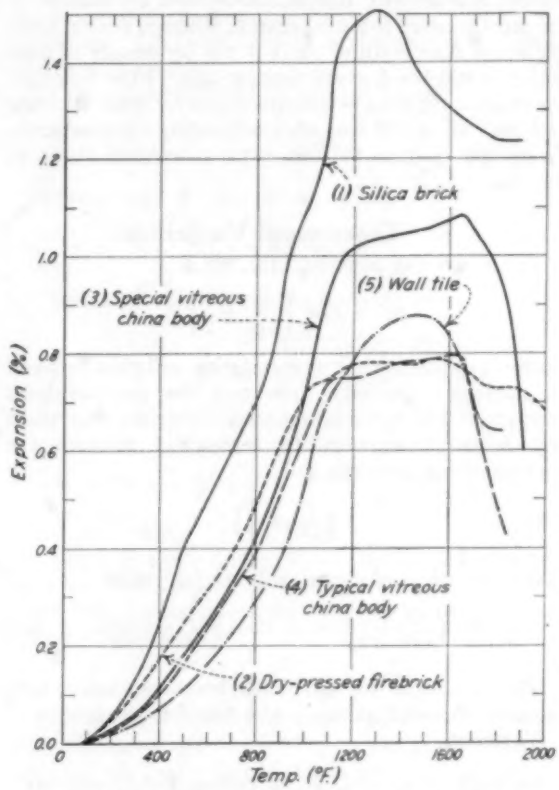


Fig. 1.—Thermal expansion of unfired material.

It was evident that the cracking took place during the firing and was in no manner caused by the treatment of the pieces before they were fired or during cooling after they were fired. The water-smoking period also seemed to be adequate.

The typical feature of the type of cracking was in their depth and form (Fig. 2). This crack was quite open on the surface of the block, and it usually pene-

* Presented at the Golden Gate Meeting, American Ceramic Society, San Francisco, Calif., August 9, 1939. Received November 2, 1939.

† The curves in Fig. 1 were charted from laboratory tests on these bodies after it had been demonstrated that it was necessary to alter the firing schedule for one particular body and to base it on this expansion behavior in order to obtain satisfactory firing.

trated only to a depth of from 1 to 3 inches toward the interior, narrowing in width as it extended deeper into the block.

As a working hypothesis, it was assumed that this type of cracking might be caused by unequal expansion or shrinkage during the firing.

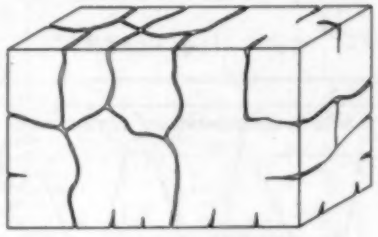


FIG. 2.—Typical cracked block.

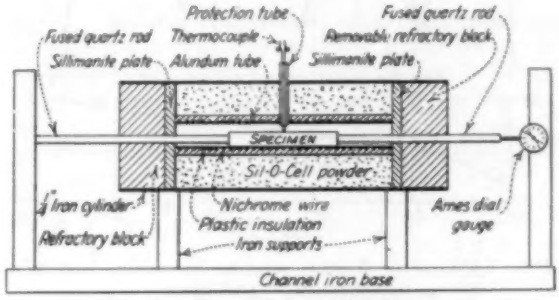


FIG. 3.—Thermal-expansion furnace.

IV. Procedure

A test piece of a well-dried green body was submitted to heat treatment in a thermal-expansion furnace (Fig. 3). Heat was applied at the rate of 200°F. per hour, bringing the temperature of the test piece uniformly to 2000°F. The expansion and subsequent shrinkage were measured by an Ames dial gauge, graduated in ten thousandths of an inch. The resulting data were calculated to percentage linear expansion and were plotted as shown on Fig. 4.

Figure 4 shows that the body expanded rapidly and uniformly to approximately 1000°F., at which point there was a sudden expansion, indicating the presence of free quartz in the body. From 1100° to 1550°F., there was a continued slight expansion; but at 1550°F., shrinkage started, and it became quite rapid at 1900°F.†

From these data, Fig. 5 was made to show the behavior of this body on being heated according to the standard schedule previously used in commercial downdraft kilns.

This expansion curve reveals the fact that there were two errors in the former firing schedule. After the furnace was heated quite slowly to 400°F., the temperature was raised at what was formerly a safe rate, but with the new body there was a rapid expansion as well as a sharp peak at the point at which the expansion of the body stopped and shrinkage began to take place.

† The heating could not be continued beyond 2000°F. with the equipment being used. It would be interesting to determine the thermal behavior during the complete firing cycle.

The cracking might have taken place during the rapid expansion or at the peak of the expansion. It seemed probable, furthermore, that owing to the lag in temperature of the interior of the block behind the surface temperature, the outer portions may have passed through the expansion period and may have begun to shrink

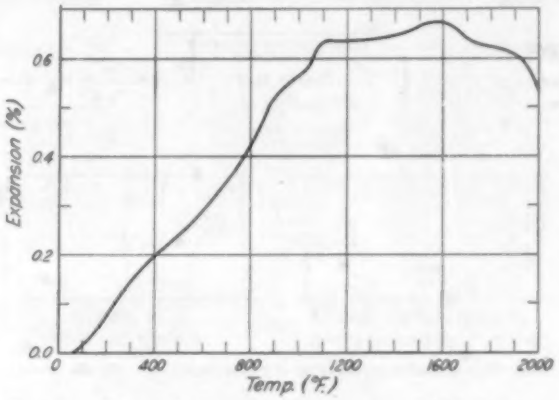


FIG. 4.—Thermal-expansion curve on well-dried green body.

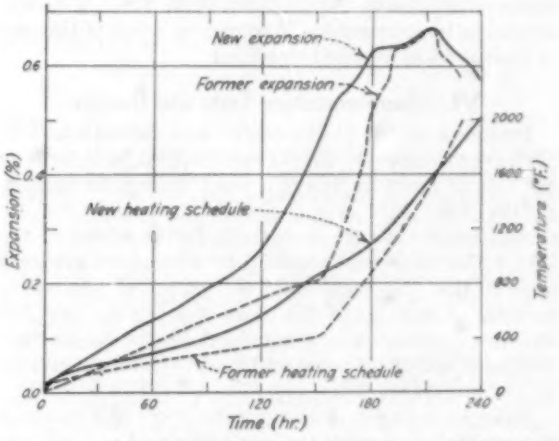


FIG. 5.—Old and new thermal-expansion and heating schedules.

while the interior of the block was still expanding. In such a case, strains would be set up in the piece which would cause the type of cracks found in the defective blocks. Figure 6 shows the manner in which the cracking is believed to have occurred.

V. Correction of Firing Schedule

A new firing schedule was planned for the block, based on the expansion and contraction behavior of the body. An ideal firing schedule is believed to be one that will produce a uniform straight-line expansion up to the point at which expansion stops, but this procedure requires more exact control than is possible in a large commercial kiln. A compromise schedule was necessary which would greatly reduce the strains in the body caused by expansion behavior.

A kiln was set with blocks and fired as closely as possible to this planned schedule (see Fig. 5).

The expansion of the body for this heating schedule was calculated from the expansion curve of Fig. 4 and is shown as the new expansion curve. It is apparent that the rate of expansion at no time is as rapid as formerly and that the peak of the curve is much broader, which would decrease the strain in the piece during the change from expansion to shrinkage.

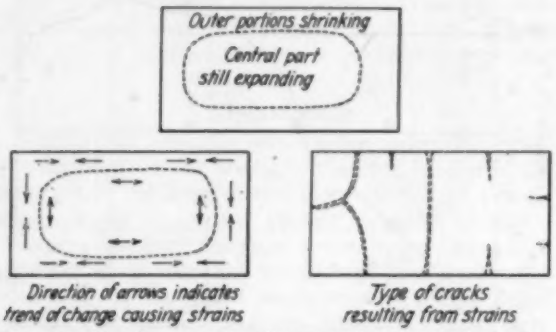

Outer portions shrinking
Central part still expanding
Direction of arrows indicates trend of change causing strains
Type of cracks resulting from strains

FIG. 6.—Cracks occurring from strains set up in body.

This new schedule did not appreciably prolong the time of firing, but there was a slightly faster increase of temperature during the first part of the fire. This was proved to be satisfactory, however, by a test of the rate of moisture loss in ware being fired.

VI. Supplementary Tests and Results

Inasmuch as the blocks placed in a commercial kiln are never completely dry, it was decided to determine the rate of moisture loss of a block during the heating of the kiln. An average block was suspended by a steel cable through an opening in the crown of the kiln. The cable was attached to a standard platform scale so that the block could be weighed at regular intervals. A portion of the block was cut out and the moisture content was determined in the laboratory. Frequent weighings were made, and the loss of weight was recorded (Fig. 7).

Relative humidity measurements were also made of the atmosphere outside the kiln to determine if this was a factor in drying the block in the kiln. These data and that of the temperature of the kiln are shown on Fig. 7. The humidity of the outside air apparently is not an important factor in drying the block in the kilns under normal conditions.

When the block had lost all of its moisture, it was lowered to rest on the other block in the kiln, and the cable was withdrawn so that the firing could proceed.

A small hole was drilled to the center of another block near the door of the kiln in which the junction of a long thermocouple was placed to measure the temperature of the center of the block during the critical periods. Another couple was placed so that its tip was just at the surface of the same block. Thus it was possible to measure the lag in temperature between the center and the surface of the block. Expansion curves were plotted for these temperatures and are shown on Fig. 8. The new firing schedule which was adopted has prevented the development of strains severe enough to crack the blocks.

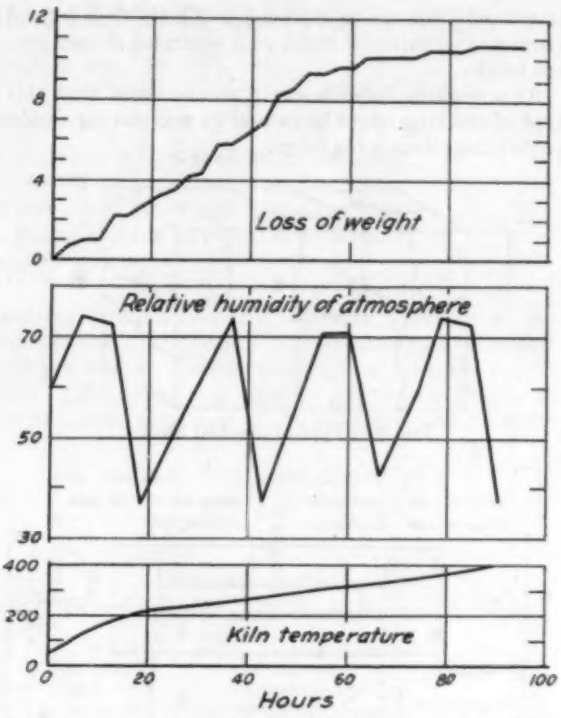


FIG. 7.—Loss of weight, relative humidity, and kiln temperature for test blocks.

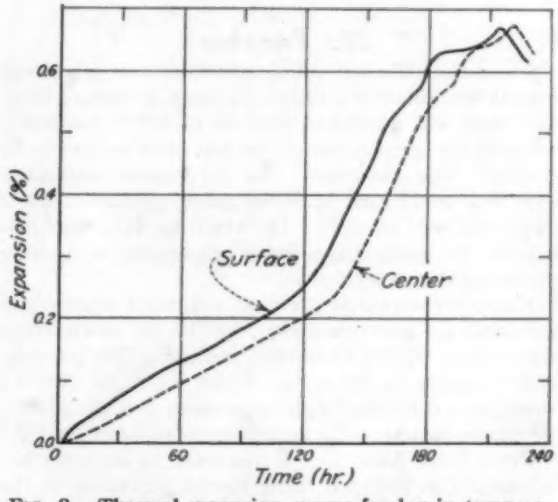


FIG. 8.—Thermal-expansion curves for lag in temperature between center and surface of block.

After the test thermocouples were removed, the firing was continued until the proper cones were brought down, and after cooling on the standard schedule, the kiln was opened for inspection. The ware was in perfect condition. The new schedule was therefore adopted as standard for firing all kilns of tank blocks. After many test firings, the results have been satisfactory, and the kiln losses have been negligible.

TILLOTSON CLAY PRODUCTS COMPANY
3363 FRUITLAND ROAD
LOS ANGELES, CALIFORNIA

CERAMIC ABSTRACTS

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AMERICAN CERAMIC SOCIETY

Ross C. PURDY, Editor

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April, 1940

19—4

Abrasives

Cutability and dressing of the grinding wheel. Heating of the workpiece in grinding. Effect of coolant. F. KÜLPMANN. *Oberflächentech.*, **16** [24] 221–22 (1939).—A correctly selected grinding wheel, i.e., one which is suitable according to material, hardness, grain size, binder, and the material it has to grind, will always resharpen itself because the grains become dull (first gradually and then rapidly), spall off, and come out of the binder, thus freeing the sharp grain underneath for new attack. This process continues until the grinding wheel is used up. The wear of a grinding wheel increases with decreasing diameter because the circumferential speed decreases, making the wheel softer. An arrangement for regulating the speed is therefore advisable to keep the circumferential speed constant. The sharpening of a wheel with diamond or special steels depends much on the speed; the time to be applied can be taken from the formula $T = [(b - s)/t] \times v^3$, where b = the width of the wheel in mm., s = the path of the sharpening device from right to left in mm., v = circumferential speed of the wheel in m. per sec., and t = the advance of the diamond in mm. per revolution. The greatest pressure occurring in grinding at the point of contact is determined by $\sigma_{max.} = P^{1/3} \times H^{1/3}/\lambda^{2/3}$, where P = perpendicular pressure, λ = a factor depending on the length of contact, and H = the function of the elongations of the bodies in contact. If the wheel is dull, the pressure can become too great and the wheel can explode. A good coolant, especially for ceramic wheels, is a solution of 1.5% soda-free soap in 98.5% tepid water. Before starting to grind, care should be taken that the wheel is saturated with the coolant. For most effective use, the coolant should be of such nature that it does not destroy the grinding wheel, the wheel should be so dimensioned that the contact arc between the workpiece and the wheel is small to obtain good cooling effect, and the coolant should come out of a nozzle in a flat jet the width of the wheel and under a pressure which keeps the surface of the wheel clean. These are determining factors for economical grinding operation. M.H.

New types of corundum rocks from the isle of Naxos (Grecian Archipelago). J. PAPASTAMATIOU. *Compt. Rend.*, 208 [26] 2088–90 (1939).—Among the granitic and muscovitic rocks of Naxos, the following new types of corundum-bearing minerals have lately been discovered which possess quite distinct mineralogical and structural properties: (1) kyschtymite, a white mineral consisting essentially of corundum and feldspar, viz., plagioclases 67.81, corundum 25.54, margarite 6.40, and tourmaline 0.25%; (2) pegmatitic kyschtymite, which contains tourmaline, corundum, plagioclase 85 to 100%, a few margarite lamellas, and small crystals of rutile and magnetite; and (3) naxite, which is a rock of pneumatolytic origin and is mainly made up of phlogopite 60, corundum 33, and plagioclases 7%; it is similar to the marundite of the Transvaal. The kyschtymite is similar to the kyschtymite of the Ural mountains but is poorer in corundum and richer in plagioclases. The possible origin of the minerals from magmatic conditions is theoretically discussed. M.H.

Preparation of grease-free polished surfaces. IAN W. WARK. *Nature*, **143** [3633] 1024 (1939).—Polished surfaces of metals and minerals are frequently required to be completely free of grease. In electron-diffraction work, for example, a film of grease causes complications and trouble. Four main sources of contamination are (1) the polishing materials (abrasives and laps of soft metal or cloth), (2) grease from fingers from handling, (3) water used in polishing and storing the mineral, and (4) airborne grease. J.L.G.

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Device for grinding eccentricity in pistons. Eric Edwin and Merle Peterson. U. S. 2,189,242, Feb. 6, 1940 (March 2, 1939).

Endless grinding and polishing belt. G. H. Cherrington. U. S. 2,189,754, Feb. 13, 1940 (April 29, 1938).

Granular coated article. H. P. Kirchner and C. E. Wooddell (Carborundum Co.). U. S. 2,187,743, Jan. 23, 1940 (April 5, 1934; April 28, 1938).

Grinder. H. A. Maurer (Oster Mfg. Co.). U. S. 2,189,015, Feb. 6, 1940 (Jan. 11, 1937).

Grinding or abrading machine. S. A. Horstmann. U. S. 2,188,947, Feb. 6, 1940 (July 9, 1938).

Grinding machine. Cincinnati Grinders, Inc. Brit. 516,887, Jan. 24, 1940 (July 16, 1937). R. H. Cramer and P. H. Hutchinson (General Motors Corp.). U. S. 2,188,675, Jan. 30, 1940 (Feb. 9, 1938). J. I. Garside and C. G. Flygare (Norton Co.). U. S. 2,190,134, Feb. 13, 1940 (June 9, 1939). Everard Stubbs (Norton Co.). U. S. 2,189,931, Feb. 13, 1940 (Jan. 27, 1939).

Grinding-machine attachment. E. F. Henry. U. S. 2,189,246, Feb. 6, 1940 (Jan. 11, 1939).

Grinding screw threads. H. Lindner. Brit. 516,259, Jan. 10, 1940 (Aug. 7, 1937).

Grinding wheel. Edward Van der Pyl (Norton Co.). U. S. 2,189,259, Feb. 6, 1940 (May 19, 1938).—The method of making a diamond grinding wheel.

Grinding wheel truing apparatus. C. C. Alvord (Norton Co.). U. S. 2,190,132, Feb. 13, 1940 (July 2, 1938).

Machine for grinding or polishing floors, etc. Aktieselskabet Fisker & Nielsen. Brit. 516,405, Jan. 10, 1940 (Oct. 22, 1937).

Manufacturing abrasive articles. Ernst Elbel and Fritz Seebach (Behr-Manning Corp.). U. S. 2,188,341, Jan. 30, 1940 (Dec. 24, 1931).—A process of preparing an abrasive article comprises applying to a flexible base abrasive grains and a binder including a heat-hardening composition of a phenolaldehyde resin brought into homogeneous solution with a drying oil and heating to cause setting of the binder to a solid film characterized by adherence, flexibility, water resistance, and freedom from softening.

Mechanism for shaping and truing the operative surface of grinding wheels used for form grinding. Coventry Gauge & Tool Co., Ltd., S. J. Harley, and G. Olah. Brit. 516,718, Jan. 24, 1940 (April 5, 1938).

Metal-bonded abrasive articles. Carborundum Co. Brit. 516,474, Jan. 17, 1940 (June 28, 1937). Carborundum Co. and W. J. Tennant. Brit. 516,702, Jan. 24, 1940 (July 5, 1938); addition to 497,006.

Metal-bonded abrasive or wear-resistant articles. Carborundum Co. Brit. 516,475, Jan. 17, 1940 (June 28, 1937).

Method and apparatus for relieving gear cutters. M. H. Johanson (Gleason Works). U. S. 2,188,005, Jan. 23, 1940 (May 15, 1937).

Portable hand buffer. G. W. Yerkey (Ed. Ball). U. S. 2,188,126, Jan. 23, 1940 (Dec. 6, 1938).

Positive stop abrading tool. K. W. Connor (Micromatic Hone Corp.). U. S. 2,188,567, Jan. 30, 1940 (March 12, 1937).

Resin-bonded abrasive article. S. S. Kistler and C. E. Barnes (Norton Co.). U. S. 2,189,733, Feb. 6, 1940 (Jan. 28, 1938). U. S. 2,189,734 and 2,189,735, Feb. 6, 1940 (Jan. 28, 1938; renewed Oct. 31, 1939).

Rotary grinding machines. N. Ahlmann. Brit. 516,-023, Jan. 3, 1940 (June 18, 1938).

Tool-dressing apparatus for bevel gear generating machines. Heinrich Schicht (W. Ferd. Klingelnberg Söhne). U. S. 2,188,016, Jan. 23, 1940 (Feb. 23, 1937).

Tool-grinding machines. F. Deckel. Brit. 516,558, Jan. 17, 1940 (March 5, 1938).

Art and Archeology

Anglo-Venetian vase. E. B. Haynes. *Connoisseur*, **104** [458] 187–89 (1939).—In establishing the date (1673 to 1676) of the vase, H. tells something of the history of Anglo-Venetian work. Of the imported craftsmen, the Dutch far outnumbered the Italian, and the Venetian styles were modified considerably. Even Verzelini glasses have enlarged bowls to suit a "deeper drinking country." The closest adherents to the Venetian styles were influenced by the new lead metal and the different technique it required. Illustrated. M.E.P.

Art of the Maya. Margaret B. Howser. *Art News*, **36** [10] 8–9, 21 (1937).—H. describes typical ceramic ware of the ancient civilization of the Maya. Illustrated. F.G.H.

Ceramics with a Yuletide flavor. Anon. *Arts & Dec.*, **51** [3] 9 (1939).—Jean Manley depicts a series of Yuletide porcelain figures. Illustrated. L.F.M.

Chinese porcelains on parade. Alfred Salmony. *Art News*, **38** [4] 7–12 (1939).—The history of Chinese porcelain is reviewed and excellently illustrated. F.G.H.

Chinese potters in review. J. Leroy Davidson. *Art News*, **36** [17] 15 (1938).—Pottery and porcelain from the collection of E. Baerwald of Berlin are described and illustrated. F.G.H.

Crystal for the table. Anon. *Verre & Silicates Ind.*, **10** [34–36] 346–47 (1939).—Excerpts from the Almanac des Gourmands, 7th year, printed by Callot, Paris, MDCCCX, are given. The use of crystal ware for the table is described in the quaint manner of the time, with the occasional introduction of advertising matter and cautions against substitutes, showing that business practices have not changed. M.V.C.

Early German art revived; historic materials used by Mrs. Keyser. Grace Ramey. *Bull. Amer. Ceram. Soc.*, **19** [2] 85–86 (1940).

English delft. Bernard Rackham. *Arts & Dec.*, **51** [3] 30, 31, 39 (1939).—Delft pottery is determined by its coating of opaque tin glaze or enamel which provides a surface for painted decoration. Before the ware has been fired and when it is in a porous absorbent state, the object is painted with great precision and rapidity. The painted design is permanently fixed in the second firing. This type of painting was limited to only four tones, blue, green, yellow, and purple. Illustrated. L.F.M.

Fundamentals of glass-container design. Darrell E. Briner. *Ceram. Ind.*, **34** [2] 42–45 (1940).—To do a good design job and produce a package which will satisfy the customer and be suitable for easy production in the plant, the designer must know (1) what type of product the container is to hold, (2) approximate retail price of the package including contents, (3) desired finished size of container, (4) dimension details fixed by customer, (5) type of decorative motif, (6) whether it is to be a single or dual-use package, (7) whether it is a lone unit or one of a family, (8) sizes, color, and shapes of all labels to be used on the package, (9) chemical nature of the product to be packed, and (10) types of bottle-forming machinery in the glass plant and the filling, labeling, and capping machinery in the customer's plant. Illustrated. L.M.C.

Glass. M. L. ANDERSON. *Architectural Rev.*, **74**, 33–35 (1933).—Many types and styles of glassware are described and illustrated. F.G.H.

Glassware. ANON. *Architectural Rev.*, **78**, 293–96 (1935).—Illustrations. F.G.H.

Lea H. Halpern, Dutch ceramist. K. ZIMMERMAN. *Bull. Amer. Ceram. Soc.*, **19** [2] 85 (1940).

Inscriptive pottery. FRANK DAVIS. *Illus. London News*, **103** [2692] 994 (1938).—A collection featuring 18th century English plates with verse inscriptions and red and green decorations is illustrated. L.F.M.

Knives with porcelain and glass handles: 18th century. ANON. *Connoisseur*, **104** [457] 163 (1939).—Six knives are shown in a full-color illustration and are labeled as follows: (1) French (Tournai?), mounted in Russia, 1790; (2) Meissen, with steel blade, water-gilt; (3) Chantilly, probably mounted in Germany; (4) Chantilly, mounted in Germany; (5) Chantilly, mounted in England; (6) Venice glass, mounted in Germany. M.E.P.

Method of designating colors. DEANE B. JUDD AND KENNETH L. KELLY. *Jour. Research Nat. Bur. Standards*, **23** [3] 355–85 (1939); R.P. 1239. Price 10¢.—A method of designating the colors of powdered drugs and chemicals and crude whole drugs is described which was devised for its applicability to colors of opaque nonmetallic surfaces. Suggestions for its extension to the color designations of transparent and translucent media are given. It is hoped that it will eventually be elaborated into a successful system of color designation for the general use of science, art, and industry. R.A.H.

Nature of pink pigment for ceramic masses. N. K. ANTONEVICH. *Zhur. Priklad. Khim.*, **11**, 1320–33 (1938). —The pink pigment is a synthetic *pinc rubin* mineral containing a small amount of Mn and is obtained from a mixture of Al_2O_3 and not under 30% of manganese phosphate calcined at over 1200° (best results are obtained at 1250° to 1325°). Manganese phosphate can be obtained by interaction of manganese chloride or sulfate with ammonium phosphate or sodium phosphate salt. Pink corundum contains not over 2% MnO. The remainder is needed in the process of formation of corundum but is superfluous in the pigment and should therefore be eliminated. The pigmenting power of pink corundum depends on its presence in the porcelain mass as a mechanical chemically inert admixture. P.B. & E.S.

Newly discovered pottery. P. DELOUGAZ. *Illus. London News*, **103** [2693] 1027, 1028 (1938).—Several specimens of painted pottery, discovered during the excavations at Khafaje, are illustrated in color. The vases are from $3^3/_4$ in. to $13^1/_2$ in. high. L.F.M.

Oriental art in the William Rockhill Nelson Gallery of Art. LANGDON WARNER. *Art News*, **32** [10] 53–60 (1933).—Pottery and porcelain from the various countries of the orient are described and illustrated. F.G.H.

Painters and sculptors in crystal. DOROTHY LEFFERTS MOORE. *Magazine of Art*, **33** [1] 34–35 (1940).—The exhibition of Steuben glass from designs of 27 eminent artists does much for the revival of fine glassmaking with emphasis on purity of metal, perfection of workmanship, and simple designs for multiple production. Copper-wheel engraving, used at Steuben as the best means of decoration, contrasts the design sharply with the clear crystal. Many of the submitted designs were difficult or unsuitable for this technique. Plate shapes proved more adaptable to many designs. Illustrated. M.E.P.

Panorama of the art of China: Drummond *objets*. MARTHA DAVIDSON. *Art News*, **35** [33] 12, 19 (1937).—Pottery from the collection of William Drummond of Peiping is described and illustrated. F.G.H.

Persian pottery of the Parish-Watson collection. MARY MORSELL. *Art News*, **32** [32] 3, 9 (1934).—Illustrated. F.G.H.

Potter's view of American potters. R. GUY COWAN. *Art News*, **35** [4] 15–16 (1936).—The various techniques employed by representative potters of America are briefly described and illustrated. F.G.H.

Pottery. HARRY TRETHOWAN. *Architectural Rev.*, **74**, 36–38 (1933).—Styles in pottery tableware are described and illustrated. See "British—," *Ceram. Abs.*, **15** [1] 3 (1936). F.G.H.

Pottery and china. ANON. *Architectural Rev.*, **78**, 288–92 (1935).—Illustrations. F.G.H.

Pre-Columbian art at the Fogg. FREDERICK R. PLEASANTS. *Magazine of Art*, **33** [2] 84–91 (1940).—Diverse art styles and techniques are described. Mosaic workers and potters are numbered among the various crafts guilds. A pottery vase (Maya culture) with engraved design representing a jaguar, from Yucatan, is illustrated. M.E.P.

Theodore Amasa Randall, 1857–1926. ANON. *Bull. Amer. Ceram. Soc.*, **19** [2] 71–73 (1940).

Silicate industries in Japan. A. SION. *Verre & Silicates Ind.*, **10** [31–33] 326–27 (1939).—The ceramic industry was originally introduced into Japan from China and Korea, and the abundance of pottery clays, the industry of the people, and the encouragement of feudal lords contributed to the prosperity of the industry. About 500 years ago Shogun Ashikaga Yoshimasa introduced the tea cult and ceremonies at Kyoto, and the possession of rare tea services became fashionable. In the peaceful epoque of the Tokugowa (1603 to 1868), ceramic art developed further, but ceramic products were not exported until well after that period. Modern scientific methods of mass production were adopted toward the end of the 19th century. The principal production centers are the Prefectures of Tokyo, Kanagawa (porcelain of Kutani), Kyoto (porcelain of Kiyomizu and Awata), Saga (porcelain of Arita), and Kagoshima (Latsuma porcelain) for art porcelain and the Prefectures of Aichi, Gifu (Mino porcelain), and Mie (Taisho Banko porcelain), which are the centers producing table services and architectural ornaments (more than 70% of the total exports of Japan). Japan has become one of the principal world producers of porcelain. The countries in North America import one third, Asia one third, and the remaining third goes to other parts of the world. The glass and cement industries have also grown in importance in Japan. M.V.C.

Survey of early Chinese art. J. LEROY DAVIDSON. *Art News*, **36** [16] 11–12, 23 (1938).—D. surveys early Chinese pottery. Illustrated. F.G.H.

Survey of later Chinese art. MARTHA DAVIDSON. *Art News*, **36** [25] 11 (1938).—Ceramics and *objets d'art* from Ming to Ch'ien-Lung are briefly described and illustrated. F.G.H.

Thirty centuries of Chinese art. MARTHA DAVIDSON. *Art News*, **35** [9] 12–13, 24 (1936).—Pottery and porcelain of many dynasties are described and illustrated. F.G.H.

Thirty-five hundred years of glass. ALFRED M. FRANKFURTER. *Art News*, **35** [3] 13–14 (1936).—Numerous museum pieces are described and illustrated. F.G.H.

Windows in Sacred Heart Chapel. CAROLINE BOUWHUIS. *Stained Glass*, **34** [3] 72–80 (1939).—The characteristics of the stained glass windows of the Sacred Heart Chapel in the German Roman Catholic Orphanage at Buffalo, N. Y., are described and illustrated. F.G.H.

BOOK

Excavations at Dura-Europos. Edited by M. I. ROSTOVTZEFF, F. E. BROWN, AND C. B. WELLES. Yale University Press. Price 44s. Reviewed in *Times Lit. Supp.*, No. 1979, p. 11 (1940).—A full preliminary report is given of the seventh and eighth seasons of work (1933 to 1935) on these excavations, which have been going on since 1928. Hellenistic, Parthian, and Roman discoveries were made. K.W.W.B.

PATENTS

Decalcomania and method of preparing. J. W. KABER. U. S. 2,190,210, Feb. 13, 1940 (Nov. 23, 1937).

Designs for:

Dish. K. S. HERPEL (Hazel-Atlas Glass Co.). U. S. 118,819, Feb. 6, 1940 (Dec. 14, 1939). J. E. SPENCE (Hazel-Atlas Glass Co.). U. S. 118,951, Feb. 13, 1940 (Dec. 18, 1939). U. S. 118,952, Feb. 13, 1940 (Dec. 19, 1939).

Drink mixing cup. LOUIS MYERS (David Gensburg). U. S. 118,725, Jan. 30, 1940 (July 31, 1939).
Flower holder. M. K. GRANT (Gladding, McBean & Co.). U. S. 118,752, Jan. 30, 1940 (March 6, 1939).
Glass. E. W. FUERST AND W. D. TEAGUE (Libbey Glass Co.). U. S. 118,620, Jan. 23, 1940 (May 23, 1939).
Pitcher. DODSON HASLUP. U. S. 118,721, Jan. 30, 1940 (July 1, 1939). J. E. SPENCE (Hazel-Atlas Glass Co.). U. S. 118,727, Jan. 30, 1940 (Nov. 20, 1939).
Plate. C. W. LEIGH (Morimura Bros., Inc.). U. S. 118,703, Jan. 30, 1940 (Nov. 30, 1939). U. S. 118,704 to 118,708, Jan. 30, 1940 (Dec. 6, 1939).
Tumbler. H. L. LISSFELT (Corning Glass Works). U. S. 118,825, Feb. 6, 1940 (July 14, 1939). WILLIAM LUNDY (Olean Glass Co.). U. S. 118,963, Feb. 13, 1940 (June 8, 1939). CHARLES SAWYER (Libbey Glass Co.). U. S. 118,650 to 118,654, Jan. 23, 1940 (Nov. 29, 1939).

Cements

Dehydration of gypsum. A. A. TURTSEV. *Izvest. Akad. Nauk S.S.S.R., Seriya Geol.*, No. 4, pp. 180–87 (1939).—In natural gypsum, hygroscopicity reaches 0.20%; in synthetic gypsum it reaches 1.24%. It changes to the semihydrate at 82°C., this being the lowest temperature at which the yield of hydrate water is possible at normal conditions. The water in the semihydrate $CaSO_4(1, {}^1/_2\text{–}0)H_2O$ has a zeolite character and separates out in the interval 82° to 200°C. The dehydrated semihydrate represents the final member of the isomorphous series. The form $CaSO_4 \cdot {}^1/_2H_2O$ is of the monoclinic type and differs structurally and optically from $CaSO_4({}^1/_2\text{–}0)H_2O$. B.Z.K.

Effects of $CaCl_2$, $AlCl_3$, and $FeCl_3$ on setting time and strength of Portland cement. KEI-ICHI AKIYAMA AND JUMPEI UNOZAWA. *Waseda Applied Chem. Soc. Bull.*, **13** [26] 1–7 (1936).—$CaCl_2$, $AlCl_3$, and $FeCl_3$ were added to the plastic 1:3 cement sand mortar (water:cement ratio 0.65), and their effects on the setting time and the strength were studied. They accelerate the setting time; even 1 to 2% of $AlCl_3$ or $FeCl_3$ causes quick setting or flash setting. The strength was also increased. The results showed that an addition of 2% of the agents is the most effective. Too large an addition decreases the strength of the mortar when stored in water for 28 days. $AlCl_3$ is the most effective agent followed by $CaCl_2$. Y.K.

Pozzuolanic cements: II, Researches on the monocalcium silicate hydrate. VITTORIO CIRILLI. *Ann. Chim. Applicata*, **28** [6] 239 (1938); *Bibliografia Ital.*, [II] **IV** [10–12] Chimica Sect., Abs. 717 (1938).—By means of the calorimeter, C. found that only one molecule of H_2O is that of crystallization in hydrate monocalcium silicate. The removal of this water took place with difficulty; it began above 130° and was completed at about 700°C. The calorimeter, optical studies, and X-ray analysis showed that hydrate monocalcium silicate began to decompose at 130°C. in bicalcium silicate and SiO_2 which recombine at a higher temperature, giving wollastonite. From the way in which monocalcium silicate decomposes, C. concludes that the molecule of water must be considered as water of constitution. V.S.M.

Pozzuolanic cements and their control. Q. SESTINI. *Cemento Armato*, No. 7, p. 125; No. 8, p. 139; No. 9, p. 159; No. 10, p. 176 (1937); *Bibliografia Ital.*, [II] **I** [1–3] Chimica Sect., Abs. 197 (1938).—The most important works on pozzuolanic cements and their control are reviewed. V.S.M.

Preparation of aluminous cement from aluminum phosphate ore: III. KEI-ICHI AKIYAMA. *Waseda Applied Chem. Soc. Bull.*, **15** [4] 15–17 (1938).—Slags obtained from aluminum phosphate ore in a large-scale experiment were not suitable for making cement because they contained too much silica. The addition of lime, gypsum, and Portland cement to the slag was unsuccessful. A. prepared several aluminous cements of low silica content in the laboratory. Pure aluminum phosphate was added to aluminum phosphate ore to increase the alumina content of the cement; lime and coke were also added. The mixture was heated to 1450°C. in a graphite crucible. The chemical and hydraulic properties of prepared cements are as follows: (E-41) SiO_2 6.44, Al_2O_3 42.50, Fe_2O_3 3.42, CaO 42.1, and P_2O_5 0.22%; strength 301 kgm. per cm.^{2}; (E-43) SiO_2 11.25, Al_2O_3 43.41, Fe_2O_3 3.39, CaO 38.81, and P_2O_5 0.73%; strength 321 kgm. per cm.^{2}. A. confirmed the possibility of making alumina cement from aluminum phosphate ore of low silica content. For Part II see *Ceram. Abs.*, **18** [1] 8 (1939). Y.K.

Properties of a mixture of Portland cement and alumina cement. KEI-ICHI AKIYAMA, KINJI UESUGI, AND KOJIRO KUWAHARA. *Waseda Applied Chem. Soc. Bull.*, **13** [28] 7–16 (1936).—The setting of a mixture of Portland and alumina cements was studied. Portland cement and *ciment fondu* were mixed in various ratios, and the setting time was measured. The mixtures containing 30 to 70% show very quick setting or flash setting. The strength of the mixture is lower than that of each cement. The addition of quicklime to alumina cement quickened the setting time. Calcium dihydrophosphate prevented quick setting and increased the strength of the mixture. The heats of hydration of the mixtures were also measured. The temperature rise of the mixture which showed flash setting was very high and the speed of heat evolution was rapid, but the total heat of evolution was less than that of alumina cement alone. Y.K.

White clay-gypsum cement. P. P. BUDNIKOV AND V. K. GUZEV. *Kommunalnoe Stroitelstvo*, **1938**, No. 9, pp. 8–14.—A cheap cement is obtained by joint grinding of clay or kaolin calcined at about 800°, $CaSO_4$ (natural or obtained from $CaSO_4 \cdot 2H_2O$ by calcining at 600°), and lime. In the setting of this cement, anhydrite hydrates under the influence of $Ca(OH)_2$; $CaSO_4$ interacts with calcined clay whose Al_2O_3 and SiO_2 are in an active state (the activity was determined in a diphenylmethane calorimeter) and forms calcium hydrosulfoaluminate and calcium hydroaluminosilicate of the composition $2SiO_2 \cdot Al_2O_3 \cdot CaO \cdot 10H_2O$. Calcium hydrosilicate and hydroaluminate are also formed. The reaction velocity depends on the Al_2O_3 content of the clay, the temperature and time of calcining, the ratio of the different components of the cement, and the gypsum modifications. P.B. & E.S.

Enamel

Advancements in porcelain enameling during 1938. F. R. ATKINSON. *Jour. Can. Ceram. Soc.*, **8**, 79–84 (1939).—Two enameling developments took place in 1938 that are considered the most important of the year. One was the development of a light-absorbing material called "Stabelite" which does not allow the reflectance and, consequently, the whiteness of the ware to go beyond a certain predetermined point, no matter how many additional coatings it is necessary to apply in order to cover up surface defects. The other, which is considered the most radical departure from regular enameling procedure that the industry has ever seen, is the development of an enamel of tremendous opacity or coverage. This type of enamel has so much opacity that it can be applied at 60% of the weight of application of superopaque enamels and result in the same white color and the same percentage of reflectance. J.G.P.

Advantages of the nickel-dip solution of the modern pickle room. H. L. COOK. *Enamelist*, **15** [7] 5–7 (1938).—The proper use of a nickel dip prevents copperheading from over-oxidized metal, promotes adherence, and decreases or eliminates fish-scaling. L.E.T.

Applying enamel ground coats by electrical deposition. A. E. Badger and Burnham W. King, Jr. *Ceram. Ind.*, **34** [2] 41 (1940).—Experiments were made to determine whether electrophoresis might be used to apply a ground coat to enameling iron with possibilities of producing thinner ground coats than those formed by dipping and of devising an automatic method of application. A commercial soft sheet steel ground coat was made up into a very thin slip and placed in a vessel near a source of 110 volts d.c. Two pieces of sheet iron were connected to the d.c. poles and dipped in the slip for various periods of time. A layer of ground coat was deposited on the sheet connected with the positive pole; the other sheet was unaffected. A dip of 3 sec. was sufficient to form a suitable ground coat. This ground coat was about 2.5 mils thick. Illustrated. L.M.C.

Basis of European enamels. Helen Hirsch. *Ceram. Ind.*, **34** [2] 60–62 (1940).—H., niece to the late Julius Gruenwald of Vienna, Austria, served as secretary to Gruenwald and to his successor, Herbert Charles Thompson, of England. Upon the death of each of these famous Continental enameling experts, she received their formulas, records, correspondence, and research data. This, the first of two articles, presents as a historical record some of Gruenwald's best formulas and interesting details about his life. L.M.C.

Box-type electric furnaces and firing equipment. W. C. Cummings. *Jour. Can. Ceram. Soc.*, **8**, 68–73 (1939).—Electric furnaces for porcelain enameling are used to a large extent in Canada. This is due largely to low cost of electric power, comparatively low cost of maintenance, and more satisfactory results. C. discusses various advantages of electric furnaces. One of the principal criticisms of the electric enameling furnace is the cost of electrical energy when used as a heating medium, in comparison with other fuels, when reckoned on a straight B.t.u. basis. To conserve some of the heat wasted in heating firing bars experiments were conducted to determine whether lighter firing bars would bring about any economy. Lighter point bars for sheet-iron firing, if sufficiently light, will heat as quickly as the ware and can be used cold without causing underfiring trouble. If lighter point bars are used with an electric furnace, the furnace temperature will not drop as much and firing time is shortened. Shorter firing time allows less time for bars to cool between firing cycles, thus saving electricity and increasing production. Working conditions are improved by the use of light firing bars as the burners do not have to work over the excess heat given off by the heavier bars. J.G.P.

Cast iron for enameling. K. Emmel. *Giesserei*, **26** [11] 285–87 (1939).—E. examined cast-iron types which could be easily enameled with a firmly adhering layer. Results showed that enamel adheres best on ferritic cast Fe, whether it is ferritic because of its mixture in production or whether it became ferritic because of treatment in service by disintegration of the carbide whereby its graphite content was increased. Castings with a pearlitic structure and very fine graphite distribution could not be enameled. Ferritic castings with a much stronger growth (8 to 9%) than that of pearlitic cast Fe (3 to 4.5%) could be enameled well, but cast Fe with little growth could not be enameled at all. C gases developing in pouring favor enamelability as they produce stronger ferrite formation in the outer quickly cooling layer of the casting. Etchings show the differences in structure. M.H.

Consistency of liquid enamels. J. E. Hansen. *Emaillerie*, **7** [6] 7–10 (1939).—Clay is indispensable for obtaining the proper suspension of enamels, and the consistency of the suspension varies according to the quantity and quality of the clay, which must be pure. Bentonite can be used because of its plastic and electrolytic properties. The choice of the electrolyte (borax, magnesium carbonate, ammonia) and the quantity to be used depend on the granulation and percentage of clay and water. Feldspar or quartz in small quantities, tin oxide, and certain other opacifiers do not affect the suspension and consistency of enamels. The quantity of water in the mill affects the consistency and the ease of working of the enamel. The consistency, dipping, and draining also vary with the fineness of grinding. Coarsely ground enamels cannot be stored long but drip faster; finely ground enamels keep their properties for a long time but take longer to drip. The best temperature to dip enamels is at 18° to 26°C.; a water-cooled vat for dipping is described. The suspension of enamels which have lost their consistency can be restored by the addition of solutions of magnesium sulfate, magnesium chloride, or sodium nitrite. Concentrated boiling borax or ammonia or ammonium carbonate is sometimes used. M.V.C.

Control mill liquor to eliminate tearing. T. D. Hartshorn. *Ceram. Ind.*, **34** [2] 50, 62 (1940).—The effects of the soluble salts in enamel mill liquor have long been known but are seldom regulated by actual plant control. H. incorporated control in his plant. The method of analysis consists in titrating the total alkalinity of a 10-cc. sample of clear mill liquor with standard acid, using methyl orange indicator, and calculating to Na_2O. The same sample is boiled to expel the CO_2, cooled, and titrated with standard caustic solution, adding neutral glycerine and using phenolphthalein to give the B_2O_3 content. In H.'s shop a fairly rapid drying schedule is maintained. Because of the tearing experienced, extra clay was originally added to increase bisque film strength. With the introduction of finely milled enamels, however, when enough clay is added to give proper film strength it interferes with the enamel set. All cover-coat enamels are therefore milled with an excess of water at least 3 days prior to use and stored in stainless steel tanks to allow settling. All clear water is then removed, and sodium nitrite is added in solution. In this way, the B_2O_3 solution is slightly lowered. The alkaline salts appear to be more efficient in hardening the enamel bisque and promoting its adherence to the fired ground coat. It is desirable to use some definite kind of control on the composition of enamel mill liquor, preferably analysis of Na_2O and B_2O_3 contents and possibly determination of the total dissolved materials by drying at 210°F. L.M.C.

Design and preparation of castings for porcelain enameling. Robert B. Schaal. *Trans. Amer. Foundrymen's Assn.*, **46**, 769 (1939).—The success or failure of enamel as a finish is vitally influenced by the design of the parts and the accuracy of their fit when assembled and by factors in the foundry, such as sand conditions, types of pattern, and treatment after molding in preparation for the enameling itself. The desirable features in the design of enameling castings are (1) careful attention to clearance and tolerances; (2) accuracy of the pattern to insure proper fit upon assembling; (3) reproduction of pattern accuracy in each casting; (4) freedom from unusual warping and buckling on heating; (5) uniform section; (6) care in selection of parting lines; (7) breaking up of large flat surfaces; and (8) elimination of sharp edges. Hairlines, poor fit, and blistering may be largely eliminated by proper design. E.J.V.

Distilled water for use in porcelain enamel. D. L. Bensinger. *Enamelist*, **15** [8] 14–17 (1938).—Rain waters are generally contaminated with solids, absorbed acids, and alkalis. Water treated through a softener is also not satisfactory due to the interchange of salts. Distilled water made in a factory still equipment or bought outside insures maximum freedom from objectionable impurities, and the added expense is fully justified. An installation of a distilled-water supply in the mill room is shown. A few simple quantitative tests to determine solids and impurities in water are given. L.E.T.

Errors in reflectance measurements of porcelain enamel surfaces. M. J. Bahnsen and L. S. O'Bannon. *Ferro Enamel Corp. Tech. Bull.*, No. 3, 30 pp. (Oct. 1, 1939).—Varying conditions which may easily contribute to difference in reflectance measurements include grinding, specific gravity, sampling, and weighing. The authors conclude that the greatest error in the usual reflectance measurements occurs in the weighing of the sample. If particularly careful work is to be done, large samples should be used, and they should be weighed as accurately as possible, kept essentially flat, sprayed with a minimum of

orange peel, and fired at correct temperatures. When such precautions are taken the data should easily be reproducible to ±0.3%. F.J.Z.

Fine milling with high opacifier additions in porcelain enamels. JOHN F. HUNT. *Jour. Can. Ceram. Soc.*, **8**, 84–88 (1939).—In an effort to realize certain advantages from fine milling, three major changes were instituted in previous work. Instead of a normal opacifier addition, a 20% addition was used. Instead of grinding to 0 gm. on 200-mesh, grinding to 1 to 2 gm. on 325-mesh was carried out. In place of the regular type of spray gun used, a combination needle, nozzle, and air cap was adopted which gave greater atomization and freedom from pitting and dusting. These changes made possible an application of an even coat of good opacity as low as 25 gm. per sq. ft. H. discusses materials and equipment used in the process, milling, application, drying and brushing, and firing and lists the advantages of the process. The subject of fine milling with high opacifier additions is the most widely discussed in porcelain enameling in the United States. The advantages given by this process should make possible greater expansion in the use of porcelain enamel. Since a thin opaque coating can now be had with this type of enamel, it should replace other non-vitreous coatings. J.G.P.

Manufacture and matching of color oxides. H. M. BRENNER. *Enamelist*, **15** [5] 5–8 (1938).—B. outlines the various steps necessary for the manufacture of coloring oxides for porcelain enamel. He discusses the methods of mixing the base coloring oxides, the best combinations to use, and the various factors which enter into color variation in enamel. Chemicals and mineral oxides for producing black, gray, blue, brown, yellow, green, red, and orange shades are listed. L.E.T.

New uses for porcelain enamel. J. T. IRWIN. *Jour. Can. Ceram. Soc.*, **8**, 89–95 (1939).—I. lists a number of new uses that have been developed for porcelain enamel and gives suggestions for additional applications for a finish that offers cleanliness, resistance to corrosion, abrasion resistance, and heat resistance. New applications include medical cabinets, telephone-booth interiors, frosted-food cabinets, washing machines, coal chutes, hot water heater tanks, chimney flue linings, etc. J.G.P.

Processes during fusion of enamels. VIELHABER. *Emailwaren-Ind.*, **16** [43–44] 252–54 (1939).—It is assumed that, during the fusion of enamel, the fluxes begin to melt first because they have a lower melting point than the refractory mineral constituents of the enamel. V. has shown, however, by a series of experiments that the melting point of a mixture of fluxes and refractory minerals may fall below the melting point of the fluxes and that the fusing point does not always rise with increasing refractory mineral content and decreasing flux content. Fluorspar is considered a good flux in additions up to 8%, though batches with 10 and 12% and more were found. This is explained by the experiments as follows: Soda is usually present in the batch to react with fluorspar, and 8% fluorspar gives a good ratio. If the soda content is raised, the fluorspar content can also be raised without affecting the action of the fluorspar, but the soda cannot be replaced by other fluxes. The fluxing action of fluoride also varies with the kind and quantity of flux present, but the proportions cannot exceed certain limits. Borax surpasses other fluxes only when used in considerably larger amounts. M.V.C.

Produce 1500 different items in southern enamel plant. ANON. *Ceram. Ind.*, **31** [2] 40–41 (1938).—The Samuel Stamping & Enameling Co., Chattanooga, Tenn., maintains its own die-fabricating department, water plant, and smelting plant and two continuous furnaces, two box furnaces, and a multitude of accessory equipment which make it a modern factory capable of producing as many as 1500 different enameled items a month. A detailed description is given. E.J.V.

Situation of the German enamel industry. VIELHABER. *Emailwaren-Ind.*, **16** [39–40] 235 (1939).—Research in the enamel industry, principally on problems relating to raw materials, has been continued, and the use of scarce materials has been reduced. Exports have been cut down. M.V.C.

Tearing of vitreous enamels. J. E. ROSENBERG AND A. F. LANGERMAN. *Jour. Amer. Ceram. Soc.*, **23** [3] 80–86 (1940).

Tellurium lead for pickling equipment. G. O. HIERS AND G. A. STEERS. *Metal Ind.* [London], **54** [4] 143–45 (1939).—Small amounts of tellurium added to lead give increased fatigue and corrosion resistance, and this results in greater life when tellurium lead is used for pickling tanks. Tellurium lead possesses the ability to be cold worked, and this property is of great advantage in preventing ballooning of heating coils. H.E.S.

Testing of the enamel layer for impermeability (denseness). V. Z. OSTROVSKIĬ. *Khim. Mashinostroenie*, **1938**, No. 2, pp. 31–32; *Khim. Referat. Zhur.*, **1** [11–12] 200–201 (1938); *Chem. Abs.*, **33**, 9570 (1939).—For the chemical determination of invisible pores and cracks in the enamel layer the surface of the enamel is liberally wetted several times with a 3% solution of KCl (several drops of H_2O_2 per 100 ml. of the KCl solution may be added). After 1 hr. the enamel surface is wetted with a solution of $K_4Fe(CN)_6$ or of NH_4CNS. In the presence of cracks or of pores, blue spots from $K_4Fe(CN)_6$ or red spots from NH_4CNS appear. Thin (hair) pores cannot be detected by this method. For their determination the electric method is used. Pour some 1% neutral NaCl solution and several drops of phenolphthalein into the vessel being tested. A milliammeter is connected to a d.-c. circuit, one end of which is connected to the anode immersed in the solution and the other end to the outer surface of the ware being tested (cathode). To obviate damage to the milliammeter, two electric bells with push buttons are connected to it in parallel (100 v. and 2 v.). The d.-c. circuit is closed with the push button of the 100-v. bell. If the bell does not ring, the 2-v. bell is connected. If no signal is obtained the milliammeter is connected to the circuit. Diagrams are given.

Testing the scratch hardness of different enamels. A. KÖNIGER. *Glashütte*, **69** [27] 465–68; [28] 484–86; [29] 499–501; [30] 515–18; [31] 531–33 (1939); see *Ceram. Abs.*, **18** [3] 70 (1939). M.V.C.

Glass

Action of arsenic on the coloring and decolorizing of glass: I. L. SPRINGER. *Glashütte*, **69** [29] 497–99 (1939).—Arsenic acts on color oxides sometimes as oxidizer and sometimes as reducer, (1) oxidizing iron oxide; (2) weakening manganese oxide; (3) causing the disappearance of a brown violet color produced by nickel oxide in a soda-lime glass; no action was observed on a cobalt blue glass; (4) displacing the yellow coloring of chromium compounds toward green; (5) reducing copper oxide; arsenic decolorized silver in a lime crystal glass, but had no effect on a lead glass; it deepened the yellow color when introduced into another glass; (6) weakening the effect of selenium; and (7) oxidizing and decolorizing sulfur and carbon compounds. No arsenic is used with rare earths. The question of the effect of arsenic on the fading of colored glasses in light is complex and depends on the amount contained and on the other constituents; the presence of lead oxide, however, tends to counteract fading. M.V.C.

Air cooling of tank blocks. W. M. HAMPTON. *Jour. Soc. Glass Tech.*, **23** [96] 108–15T (1939).—H. attempts to calculate the temperature distribution through tank blocks for certain assumed temperatures within the tank and outside it. The basis of the calculation is that the three qualities of heat, (*a*) that transferred to the inner surface of the blocks, (*b*) that conducted through the blocks, and (*c*) that dissipated from the outer surface of the blocks, must be equal. Relative measurements are given for the rate of corrosion of refractories at different

temperatures, and from these and the calculated temperatures an estimate of the change of thickness of the blocks with time is obtained by numerical integration. The calculations suggest that forced air cooling is of no value in the early stages of the life of a tank and makes relatively small difference in the temperature of the inner surface, even when the blocks are considerably reduced in thickness. G.R.S.

Air filters manufactured out of glass wool. ANON. *Gesundh.-Ing.*, **61** [3] 41 (1938).—Experiments made with American and Russian glass wool for air filters are described. Results are given and compared. See "Air Conditioners—," *Ceram. Abs.*, **19** [1] 19 (1940). W.D.K.

Attempt to correlate some tensile strength measurements on glass. JAMES BAILEY. *Glass Ind.*, **20** [1] 21–25; [2] 59–65; [3] 95–99; [4] 143–47 (1939).—The pertinent data required are listed. B. assumed that the measured strength depends upon the character of the flaws, that these flaws magnify the applied stress, and that breakage occurs when the stresses at the apexes of the flaws reach a certain maximum value. An attempt is made to derive a relation between the strength and the stressed areas in one lot of test pieces. The effect of testing several short specimens instead of one long specimen is shown, indicating how the strengths vary due to variation in flaw distribution in the specimens. Considerable data on the area-strength relation are presented. The flaw is defined as a discontinuity in the structure which controls the strength of the whole and which affects the strength in proportion to its size and to its orientation with respect to the direction of stress. The works of Black (*Bull. Amer. Ceram. Soc.*, **15** [8] 274–75 (1936)) and Preston (*Jour. Amer. Ceram. Soc.*, **18** [7] 220–24 (1935)) are selected for the discussion of the strength-time relations, and the data obtained by these workers are studied. Much of the data on the tensile strength of commercial lime glass can be correlated by taking into account the three major factors, viz., (1) the relation between stressed area and the flaw pattern, (2) the character of the flaws which determine the stress level, and (3) the rate of stressing. If the type of test piece varies widely, an additional factor which appears to be a kind of orientation must also be considered. Various kinds of surface treatment, such as acid polishing, appear to change the level of stress without altering the flaw pattern or otherwise changing the behavior of the glass under test. Surface compression due to lack of annealing must be corrected for unless this is very small. The assumption that the breaking effect of a stress is proportional to the time of application of the stress and inversely proportional to the breaking time at that stress is substantially in agreement with the findings of Black and Preston, and a method of applying this to the solution of various strength-time data is given. Certain factors involved in testing are discussed. E.J.V.

Automatic pressure-control systems for flat glass tanks. R. L. SHUTE. *Ceram. Ind.*, **31** [2] 42–44 (1938).—S. discusses the accurate operation of glass furnaces by pressure, taking up the problems originally encountered and overcome by improvement of equipment used. He presents data on tests made and points out that the best location for the pressure-control point is on the side wall of the furnace, between the last port and mid-section, 12 in. above the glass level. E.J.V.

Coloring of green bottle glass and influence of color on workability. A. DIETZEL. *Glastech. Ber.*, **17** [11] 303–306 (1939).—The action of MnO_2 in bottle glasses is due to its high oxygen content which is partially liberated at melting temperatures and partly used in converting FeO to Fe_2O_3. There is a corresponding color change from blue-green to yellow-green. This is accompanied by improved thermal transmission through the glass during melting and lower heat radiation during working as shown by relative radiation measurements. Other oxidizing agents such as As_2O_3 and CeO_2 have essentially the same effect as the MnO_2. J.F.H.

Color tint of glass and the shortage of raw materials in Germany. ANON. *Sprechsaal*, **72** [49] 574 (1939).—The simplest way to meet the shortage of domestic decoloring agents is to encourage the use of more iron-green glass (not decolorized) for as many purposes as possible. M.V.C.

Comparison of the rates of melting of glasses made from sodium carbonate, dolomite limestone, and silica sand. J. C. POTTS. *Jour. Soc. Glass Tech.*, **23** [97] 129–40T (1939).—Using the disappearance of batch as a criterion, a comparison of the rates of melting of a series of glasses was made by two methods. Both methods gave substantially the same results. The glasses were made from soda ash, dolomite limestone, and silica sand. The composition range studied was 10 to 18 Na_2O, 8 to 22 (CaO + MgO), and 63 to 80% SiO_2. G.R.S.

Cooling of flat glass. HIDEO YAMAMOTO. *Glastech. Ber.*, **17** [11] 301–302 (1939).—Flat glass prepared by the Fourcault and the Pittsburgh vertical draw processes was examined by means of a polariscope. The Fourcault glass showed noticeable strain only in narrow uniform bands along the edge; in the Pittsburgh glass the bands were broader and the strain was frequently found in the center. The temperature distribution was determined during operation by contacting the glass at various points with a thermocouple, thus making it possible to control cooling conditions better. J.F.H.

Distribution of temperature in molten masses of colored and colorless glasses. R. HALLE, ERIC PRESTON, AND W. E. S. TURNER. *Jour. Soc. Glass Tech.*, **23** [97] 171–96T (1939).—Preliminary measurements of the cooling rates of the different glasses showed that the colored glasses examined had a higher radiation power than a colorless glass of similar composition. The emissivity of these glasses depends not only on their color, but also on the concentration of the coloring agent present in the glass. Arranged in decreasing order of radiation power, the glasses are a dark iron-manganese amber containing 4.6% Fe_2O_3 and 5.1% MnO_2, a green iron-manganese glass containing 1.57% Fe_2O_3 and 2.3% MnO_2, a light iron-manganese amber glass containing 2.88% Fe_2O_3 and 3.28% MnO_2, and a carbon-sulfur amber glass containing 0.2% Fe_2O_3. To determine the vertical temperature gradient of a molten mass of glass, an experimental rectangular tank holding 45 lb. of glass and having a depth of 5 in. was constructed; when thermal equilibrium had been obtained, a thermocouple was lowered into the molten glass and the temperatures were measured at different depths in increments of $^1/_2$ in. The order in which the temperature gradients of the glasses increase with increasing depth is, in all cases, colorless, carbon-sulfur amber, and iron-manganese green glass. Convection currents do not appear to play an important part in the heat transfer under the test conditions employed. The difference in temperature distribution in a molten mass of colorless, amber, and green glass appears to be only a function of the different diathermancies of these glasses. Colorless glass transmits radiant heat effectively; the amber and green glasses are strong absorbents of infrared radiation. This is confirmed by the tests in which the gas consumption was kept constant. In the surface layers, the colored glasses attain a higher temperature than the colorless glass, but from a depth of 1.5 in. downward the order is reversed, showing that, due to the greater absorptive power of the colored glasses in the upper layers, less heat penetrates into the body of the glass to heat the lower layers. G.R.S.

Durability of glass—estimating dissolved alkali by pH determination. R. F. DORAN AND S. R. SCHOLES. *Jour. Amer. Ceram. Soc.*, **23** [3] 91–92 (1940).

Elastic properties of vinyl sheeting. S. BATESON. *Jour. Applied Physics*, **10**, 887–89 (1939).—Plasticized vinyl sheeting used for the manufacture of safety glass was elongated under constant load. Upon unloading the specimens below 50°C., recovery was complete. Creep is pronounced during both extension and recovery. Elongation and birefringence are not strictly proportional, which suggests that most of the orientation takes place during the initial elastic extension and only slightly during the aftereffect. A.P.

Fining, decolorizing, and coloring of glass within the restrictions of "Reichstelle" chemistry in Germany. K. O. HAHNEL. *Sprechsaal*, **72** [48] 559–60 (1939).—The deficiency of certain chemicals in Germany has created changes in the three large branches of glass production, viz., fining, decolorizing, and coloring. Because of the scarcity of arsenic the problem of fining glass is met by various other means, e.g., changes in the method of fusing, increased soda content, or increased carbonic acid lime; new ways of replacing the arsenic used for fining by antimony, saltpeter, or the new barium saltpeter, which is more powerful than potash or soda saltpeter, are mentioned. The chemical function of antimony oxide is analogous with that of arsenic. Glauber's salt has a similar action when used in sufficient quantities. The use of sulfate and saltpeter for fining and decolorizing is known; two other large groups, the chlorides and the ammonium salts, are discussed. The action of these substitutes is explained. In all cases where a light, white glass is desired, the fundamental requirement is the use of raw materials which contain as little iron as possible or those in which the iron has been reduced by pretreatment. Baryta may partly replace marble powder in some cases; aluminum hydroxide must be used in place of the less pure feldspar for high quality glass. Chemical decoloration can be brought about by (1) supersaturating the glass with oxygen so that the dissociation of the trivalent iron is retarded by SO_3, N_2O_5, CeO, BaO_2, and Sb_2O_5, (2) complex iron combinations, by which means the dissociation is lowered or a complex form is obtained which has a different color-absorption range from the coloring forms, and (3) converting the color oxide into salts which are not dissociated in the melt. Such nondissociating compounds can be found where equivalent acids occur with equivalent cations. The oxidation of the darker blue-green ferrous oxide into the ferric form and the use of fluorides are discussed. Phosphate is used as an oxidizing agent and as a complex producer. The effect of sodium chloride with selenium in decreasing the iron oxide content in glass is explained. Nickel oxide can be used to neutralize residual color tones of iron oxide in ordinary glass. In coloring, the chief agent to be replaced is pyrolusite; graphite has been found suitable as well as chrome oxide–nickel, chrome oxide–copper oxide–iron oxide, and iron oxide–graphite–chrome oxide. Black glasses are colored by iron sulfide. M.V.C.

Fluorbarite in flint-glass batches. ANON. *Ceram. Ind.*, **34** [2] 52–54 (1940).—Use of smaller than normal quantities of decolorizer in flint-glass batches has been achieved at the Pennsylvania Bottle Co. plant by introduction of fluorbarite as the main flux. A batch based on 750 lb. of sand uses 11½ lb. of fluorbarite to replace a previous addition of 22½ lb. of glassmaker's "Barium B" mix which is composed chiefly of barium sulfate. The new material is a very powerful flux and allows the glass to be melted at lower temperatures than those previously used. This materially increases the effective capacity of the tank. When barium sulfate mix was used, a minimum of 9 oz. of selenium was needed for the 750 lb. sand batch, and even 12 or 15 oz. were sometimes required. This selenium content has been cut to 5 oz. by the use of fluorbarite; this cuts raw material cost and produces a glass more easily controlled as far as quality standards are concerned. Illustrated. L.M.C.

Glass braider demonstrates weaving principles. R. M. SCOTT. *Machine Design*, **11** [12] 29–31 (1939).—S. describes in detail the construction of glass braiders. Wiring diagrams are given. Illustrated. J.M.N.

Glass in construction and decoration. RAYMOND MCGRATH. *Architectural Rev.*, **85** [507] 100–108 (1939).—Recent developments are reviewed under the following headings: (1) decoration processes, (2) decorative technique, (3) rolled opal glass, (4) plate and toughened glass, (5) glass brick, (6) glass and concrete, and (7) glass and steel. Illustrated. See *Ceram. Abs.*, **17** [9] 305 (1938). F.G.H.

Glass-fiber insulation. A. Y. STIRRAT. *Elec. Times*, **95** [2485] 854–56 (1939).—"Continuous" glass yarns for electrical insulation have a smooth, shiny appearance and are usually, though not always, impregnated with varnish to increase their resistance to abrasion. The thicker "staple" glass yarns are not used in the electrical industry. Glass-fiber insulation is employed chiefly in electric motors and permits higher operating temperatures to be reached with safety; size and weight can be reduced. Other applications of glass-fiber insulation are discussed in detail. J.C.C.

Glass grinding and its possibilities for sheet glass. HANS MODEL. *Glashütte*, **69** [26] 452–53; [27] 468–69 (1939).—Illustrations of window panes and hollow glassware which have been decorated with animal and floral studies or simple dots and lines ground in the glass indicate the many possibilities for adapting this type of hand decoration in architecture and for other purposes. The new decorative grinding of sheet glass grew out of the technique of hollow glass grinding with the development of hand motor grinders and similar easily manipulated tools. A pane of glass, e.g., 2 sq. m. in size and 8 mm. thick, is placed firmly and carefully in a supporting frame. A sketch is drawn on the glass with a wax pencil, preferably by the glass grinder himself. Since water must flow over the glass during grinding to prevent the glass from becoming too hot, the design must first be cut in the glass with a fine-grained marker. The design is then ground with silicon carbide, the picture is smoothed up and worked over with a finer wheel, and the whole is polished with pumice stone. The glass is not transparent but admits light. M.V.C.

Glass industry in Italy. DE BENEDETTI. *Verre & Silicates Ind.*, **10** [34–36] 348–50 (1939).—The development and expansion of the glass industry in Italy in the past 15 years are reviewed. M.V.C.

Glassmaking. M. L. ANDERSON. *Architectural Rev.*, **73**, lviii–lxiv (Feb., 1933).—A. describes the manufacture of window glass and plate glass. Illustrated. F.G.H.

Glass thermometers. J. MARTERET. *Documentation Sci.*, **7**, 50–56, 81–90 (1938); *Chem. Abs.*, **33**, 8453 (1939).—M. describes the manufacture of glass thermometers, emphasizing the care necessary to obtain uniformity of capillary cross section. Attempts to make precision thermometers with long spaces on the stem for each degree interval have not been successful, because when the capillary is less than 0.08 mm. in diameter, the errors introduced by capillarity and nonuniformity of capillary are too great. For this reason dropping chamber and auxiliary scale types of thermometers were developed by Walferdin, Roberteau, Beckmann, Kuhn, and Siebert; these are described by M.

Heat flow in a glass furnace. OTTO T. KORITNIG. *Glashütte*, **69** [32] 548–51 (1939).—The determination of the quantity of heat transferred to the melt in pot furnaces and in tank furnaces is difficult because the following three temperatures exert an influence on the melt: (1) the variable heat from the fuel source, (2) the reflection from the furnace walls and ceiling, and (3) the heat of the melt itself. Temperature measurements with a pyrometer may not be correct because numerous factors such as the position of the instrument with reference to the gas flow, the conditions at the beginning and ending of temperature measurement, and the duration of temperature measurements condition the accuracy of measurements. Equations are given for the theoretical calculation of heat loss by absorption of heat by furnace masonry and radiation, heat transference (3 types), emissive power of walls and charge, and the heat penetration figure. As these factors depend on the type of fuel, excess of air for firing, temperature of the heating gases, type of furnace masonry, and size of the furnace, the difficulty of accurately determining the total heat transference is understood. The theoretical calculations have a practical value, however, for the study of improving furnace construction and the comparison of furnaces fired with different types of fuel. M.V.C.

Melting glass at 5½ sq. ft. per ton. ANON. *Ceram. Ind.*, **34** [2] 37–38 (1940).—At the Wightman Bottle & Glass Mfg. Co. plant, a regenerative end-port melting

tank has been operating for over 20 months at a melting rate of one ton of glass per day for each $5^1/_2$ sq. ft. floor area in the melting end. This rate is faster than that generally used for flint glass. Rapid melting is partly due to the method of firing in which flame is introduced through two sets of burners placed in the top of the tank at the point where the ports adjoin the melting chamber. Two burners are used for each port, firing natural gas on a 15-min. cycle and using a total of 685,000 cu. ft. per day for melting 85 to 88 tons of glass. Burners are slanted down into the tank, allowing the flame to contact raw batch while it is still close to the end wall. The burners are easily placed in service, and efficient conditions are obtained without the constant adjustment ordinarily needed. Glass is being pushed through the tank in good time; thus the time available to oxidize the batch is comparatively limited. This decreases the amount of decolorizer needed. The tank is particularly economical regarding fuel. Because the burners are firing under a pressure sometimes as high as 4 lb. per sq. in., a substantial type of shadow wall is used in place of the open checkerwork usually found in regenerative tanks. Where the usual shadow wall is located directly over the center of the cover plates, two walls are used in this tank; these are placed so that their weight is carried by the front wall of the melting chamber and the rear wall of the refiner, without any great amount of weight being supported directly by the cover plates. The shadow walls were built up of silica brick laid up without mortar. After about 3 weeks of operation, however, the heat of the tank fused them together so that each wall is monolithic. Illustrated. L.M.C.

Metallurgical study of cast-iron glass molds. W. H. Bruckner, L. R. Kovac, and A. B. Wilder. *Bull. Amer. Ceram. Soc.*, **19** [2] 58–61 (1940).

Recent applications of Plexiglas. Anon. *Verre & Silicates Ind.*, **10** [31–33] 327–28 (1939).—Plexiglas is a new thermoplastic material belonging to the group of acrylic resins. Liquid and transparent acrylic products are made by long and complicated processes from wood, coal, and lime. These liquids are transformed by polymerization into solid, clear masses with a tenacity, resistance, chemical stability, and inalterability superior to those heretofore obtained with synthetic resins. Transparency is 99% with negligible loss by reflection. Plexiglas is the first organic substance which can be used for optical devices with an arbitrary number of diopters. Plexiglas can be shaped, molded, and carved as easily as ivory, and this permits multiple and novel realizations in the domain of art and jewelry making. Plexiglas is half as heavy as ordinary glass which is a substantial advantage in the construction of airplanes and automobiles. Resistance to bending from impact is about seven times greater than that of window glass. When it breaks (only under exceptional circumstances), large pieces without sharp edges are formed. Plexiglas is flexible even at low temperatures, and it is difficult to burn. It can be sawed, filed, drilled, welded, bored, and engraved with tools for working metals. The many uses of Plexiglas in industry, medicine, chemistry, etc., and its physical properties are given. M.V.C.

Otto Schott and the Carl Zeiss Foundation in Jena. Herbert Kühnert. *Glastech. Ber.*, **17** [11] 306–309 (1939). J.F.H.

Slag wool. Harold A. Bevens. *Jour. Can. Ceram. Soc.*, **8**, 17–22 (1939).—B. gives the history, manufacture, and commercial uses of slag wool. Mineral wool is an ideal material for the prevention of heat losses through the roofs of buildings; where it can be applied to walls as in frame or brick veneer construction it is equally effective. A highly acoustic material is now being made into rigid acoustic boards and tile. J.G.P.

Surface change of glass in different gases at high temperatures. I. Sawai and I. Kubo. *Z. Anorg. & Allgem. Chem.*, **232** [4] 423–26 (1937).—An oval rod of glass was heated in a stream of CO_2, SO_2, air, and in still air. Its change of form was measured and any change in the surface was noted. See "Softening—," *Ceram. Abs.*, **17** [8] 275 (1938). W.K.

Zinc oxide in the glass industry. A. Foulon. *Tech. Blätter*, **29**, 17 (1939); *Chem. Abs.*, **33**, 7505 (1939).

PATENTS

Apparatus for making containers from glass tubing. J. Dichter. Brit. 516,627, Jan. 17, 1940 (July 1, 1937).

Apparatus for manufacturing glassware. T. F. Pearson (Crown Cork & Seal Co., Inc.). U. S. 2,190,042, Feb. 13, 1940 (Jan. 11, 1937).

Apparatus for tempering glass. T. R. Crowley (Libbey-Owens-Ford Glass Co.). U. S. 2,188,401, Jan. 30, 1940 (June 15, 1937).

Coloring glass fibers, etc. N. V. Mij. tot Beheer en Exploitatie van Octrooien. Brit. 516,826, Jan. 24, 1940 (July 16, 1937).

Forehearth for and method of controlling the temperature and condition of molten glass. G. E. Rowe (Hartford-Empire Co.). U. S. 2,189,271, Feb. 6, 1940 (April 16, 1937).

Glass beveling machine. Anthony Macellaro and Anthony Tornese. U. S. 2,187,748, Jan. 23, 1940 (Oct. 1, 1938).

Glass-metal seal. Ernst Waldschmidt (Fides Ges. für die Verwaltung und Verwertung von gewerblichen Schutzrechten m.b.H.). U. S. 2,190,302, Feb. 13, 1940 (March 18, 1939).

Glass-shaping machines. W. B. Mitchell. Brit. 516,467, Jan. 17, 1940 (June 30, 1938).

Grinding tool. L. B. Lent and J. D. Gamble. U. S. 2,188,365, Jan. 30, 1940 (Dec. 7, 1937).—A tool or lap for accurate grinding to predetermined form of the curved surfaces of glass lenses, etc.

Kiln. J. T. Littleton, H. R. Lillie, and W. W. Shaver (Corning Glass Works). U. S. 2,188,608, Jan. 30, 1940 (Oct. 7, 1937).—In combination with a kiln for heating glass, a highly refractory, soft, finely divided, water-soluble substance distributed over the floor of the kiln.

Laminated safety glass. J. D. Ryan and G. B. Watkins (Libbey-Owens-Ford Glass Co.). U. S. 2,188,395, Jan. 30, 1940 (June 13, 1934).

Lens system. F. W. Gehrke and Robert Tiedeken (Agfa Ansco Corp.). U. S. 2,187,780, Jan. 23, 1940 (April 19, 1938).

Making articles of fused silica. R. D. Smith (Corning Glass Works). U. S. 2,188,121, Jan. 23, 1940 (Dec. 11, 1936).

Method and apparatus for making glass wool. J. H. Thomas, Ed Fletcher, and F. W. Atkinson (Owens-Corning Fiberglas Corp.). U. S. 2,189,822, Feb. 13, 1940 (Jan. 17, 1936).

Method and apparatus for melting rock and making products therefrom. E. R. Powell (Johns-Manville Corp.). U. S. 2,190,271, Feb. 13, 1940 (Jan. 21, 1937).

Nonshattering glass. Iwan Ostromislensky (Carbide & Carbon Chemicals Corp.). U. S. 2,189,293, Feb. 6, 1940 (Jan. 3, 1928).

Purification of silica sands, etc. Rockware Glass Syndicate, Ltd., and F. W. Adams. Brit. 516,880, Jan. 24, 1940 (July 11, 1938).

Template for edging lenses. F. E. Wolf. U. S. 2,190,582, Feb. 13, 1940 (June 30, 1938).

Structural Clay Products

Bonding of brickwork. P. M. Stratton. *Architectural Rev.*, **79**, 240–46 (1936).—The various types of bond used in England are described and illustrated in detail. Jointing or pointing materials and technique are also thoroughly discussed. F.G.H.

Government housing assistance. F. W. Nicolls. *Jour. Can. Ceram. Soc.*, **8**, 10–17 (1939).—N. explains and discusses the recent Home Improvement Loans Guarantee Act and the National Housing Act. J.G.P.

Production of face brick at Kiev plants in 1938. V. Ya.

YABLONOVSKIĬ. *Keramika*, **1939**, No. 2, pp. 17–25.—Y. describes raw materials, production processes, and the finished product. P.B. & E.S.

Progress of brick through English history. R. P. ROSS WILLIAMSON. *Architectural Rev.*, **79**, 197–228 (1936).—The history of brick manufacture in England is described in detail. Illustrated. F.G.H.

Varieties and manufacture of brick. J. K. WINSER. *Architectural Rev.*, **79**, 229–39 (1936).—All of the many types of English building brick are described and illustrated. Methods of manufacture are briefly discussed. F.G.H.

Vitrified brick and salt glaze. W. SCHUEN. *Tonind.-Ztg.*, **63** [31] 357–59 (1939).—After discussing previous work on salt glazing, S. presents the results of his own research. To facilitate the glazing of vitrified brick which may have too low a silica content or vitrify at too low a heat, mixtures of salt with other chlorides were tried. Chlorides of calcium, magnesium, and potassium in the mixtures were not successful, because the mixtures fuse and attack the body severely. Lithium chloride was only slightly better. Chlorides of lanthanum, cerium, manganese, and iron mixed in equal amounts with salt produced good coats of glaze. Ferric chloride was tried in an industrial kiln with good results. Chlorides of iron, manganese, and cerium may therefore be used to make possible the application of a salt glaze to vitrified brick, but in each case careful trials should be made. W.K.

PATENT

Brick or blocks for general building and for furnaces. L. T. MAKRAM. Brit. 516,873, Jan. 24, 1940 (July 6, 1938).

Refractories

Calorimetric method of controlling the quality of metallurgical magnesite. P. P. BUDNIKOV AND L. G. GULINOVA. *Byull. Vsesoyuz. Khim. Obshchestva*, **1939**, No. 7, pp. 14–16.—The authors investigated the relation between the calcining temperature (up to 1700°) of dolomite and lime and the amount of heat evolved when interacting with water and the relation between the calcining temperature of magnesite and the heat evolved during the dissolving of the components. A diphenylmethane Bunsen type calorimeter was used. Not only the quality (activity) of the product but also the temperature to which the material of the given composition had been calcined can be determined by this method from the thermal effect of the hydration of CaO and calcined dolomite or that of the dissolving of magnesite in HCl. P.B. & E.S.

Chemically resistant refractory material for kilns producing sodium sulfide. P. P. BUDNIKOV AND K. M. SHMUKLER. *Zhur. Priklad. Khim.*, **12**, 367–70 (1939).—The authors investigated grog brick prepared in the usual way and a forsterite brick obtained from a batch consisting of dunite calcined at 1450°, caustic magnesite, and molasses, mixed with a 12.5° Bé solution of $MgCl_2$ and calcined at 1500° to 1600°. Forsterite brick possesses a high resistance to Na_2S melts and should be regarded as the best refractory material for kilns producing this chemical. P.B. & E.S.

Creep of refractory materials at high temperatures and its bearing on the performance of glasshouse pots. J. H. PARTRIDGE AND G. F. ADAMS. *Jour. Soc. Glass Tech.*, **23** [97] 141–53T (1939); see *Ceram. Abs.*, **18** [7] 183 (1939). G.R.S.

Development and preliminary studies of pinite. G. A. PAGE, F. F. RAINE, AND V. R. SULLIVAN. *Jour. Amer. Ceram. Soc.*, **23** [3] 71–77 (1940).

Exfoliation of vermiculite by chemical means. R. C. GROVES. *Nature*, **144** [3647] 554 (1939).—G. reports that the exfoliation of vermiculite, normally produced by heating the material, can also be brought about by treating it with hydrogen peroxide (20 volume strength H_2O_2). The chemically produced exfoliation may possibly be due to the evolution of oxygen between the mineral flakes. Chlorine from a permanganate-hydrochloric acid solution causes a certain amount of exfoliation but not to as marked an extent as H_2O_2. J.L.G.

Fire and materials of construction. Refractory concretes and cements. A. ROUX. *Recherches & Inventions*, **19**, 4–11 (1939); *Chem. Abs.*, **33**, 7508 (1939).—Cyclopes brand refractory cement, used for the construction of a concrete furnace roof, for concrete test pieces for crushing tests, and for embedding iron beams was tested. The results showed this brand to be equal to other good refractory cements and superior to ordinary cements.

Grog masses for glass pots and tanks. OSKAR LECHER. *Glashütte*, **69** [31] 529–30 (1939).—In tanks, grog with high alumina content resists the molten glass better than block with a high silicic acid content because the protective layer formed between the glass and the block is more viscous, adheres better, and is, therefore, not as easily absorbed by the glass in the form of streaks and stones. Special care in the working and firing of masses is required to prevent the formation of cracks in the block because cracks facilitate the penetration of the glass into the block and hasten disintegration. The compositions of German tank block and pot clays are given. M.V.C.

Pinitized tuff of ceramic importance. P. F. KERR. *Jour. Amer. Ceram. Soc.*, **23** [3] 65–71 (1940).

Plastic refractories. J. F. MCMAHON. *Jour. Can. Ceram. Soc.*, **8**, 29–47 (1939).—McM. presents the results obtained from an investigation in the Ceramics Laboratories of the Dept. of Mines and Resources of Canada conducted to obtain information on the various properties of plastic refractories on the market so as to have a basis for formulating purchasing specifications for the Government. The tests included determination of workability, water, clay substance, and nonplastics (%) and linear drying shrinkage, dry strength, firing and fired properties, absorption, fired strength, and P.C.E. Criteria which should receive consideration in setting specifications are listed under the following headings: workability, water/clay ratio, clay content, nonplastics, linear drying shrinkage, dry strength, total shrinkage, firing shrinkage, absorption, fired strength, and P.C.E. J.G.P.

Present application and possible future development of blast-furnace refractories. W. R. MCLAIN. *Bull. Amer. Ceram. Soc.*, **19** [2] 62–68 (1940).

Properties of sagger masses from different clays. R. T. MAKHL. *Keramika*, **1939**, No. 3, pp. 18–23.—Sagger masses can be classified by their SiO_2 content, by the content of particles over 0.01 mm., by their total shrinkage at cone 35, and by their water absorption at cone 35 into groups containing 55, 55 to 62, and over 62% SiO_2 and under 5%, 5 to 15%, and over 15% of particles over 0.01 mm. and having a water absorption capacity under 2.5%, 2.5 to 4%, and over 4% and a total setting at cone 35 of 9.0 to 12.5%, 12.5 to 15%, and over 15%. Clays of the third group are less satisfactory. The existing methods of determining the spalling resistance of sagger clay are unsatisfactory. P.B. & E.S.

Slag penetration in refractory block. T. SCHAUER. *Sprechsaal*, **72** [47] 553–54 (1939).—Tests were made on refractory brick of different composition to study the phenomenon of scorification. S. observed that (1) slag disintegrates when it penetrates into the brick, (2) compounds containing iron generally penetrate only the surface, (3) porous brick in many cases may become more resistant when scorified than compact brick because of the solidification of the slag in the brick, and (4) refractory brick acts as a diaphragm which divides off the slag mixture. M.V.C.

SEPARATE PUBLICATIONS

Shamva Mullite. MULLITE REFRACTORIES CO., Shelton, Conn. 50 pp. Free.—This catalogue is devoted

chiefly to illustrations of typical applications of mullite in electric induction and arc furnaces, industrial boilers, open flame and crucible furnaces, glass tanks, ceramic kilns, iron and steel furnaces, and many other installations. It is commonly known as the "3300°F." refractory. Shamva mullite is claimed to have high softening point, low coefficient of expansion and contraction, indifference to thermal shock, imperviousness to slag erosion, negligible tendency to vitrify, ample load-bearing capacity, and chemical neutrality. Mullite air- and heat-setting cements are also described.

Steam Boiler Masonry Installation. R. Rasch. VDI, Brosch Co., Berlin, 1939. DIN A 5, 44 pp., 29 illustrations, 7 tables. Price 2.50 Rm.—The fundamental problems in the practice of furnace construction and boiler masonry installation are presented. All refractory building materials are classified, and their application, appropriate installation, and care are dealt with. The term "refractory" and the properties of the brick and their requirements in the furnace are explained so that when brick are ordered, the index of the quality required is clearly comprehensible. As the formerly employed "conventional" standards did not correspond to the requirements for a given brick, the indexes of quality for refractory building material are of special interest to the purchasing agent. Defects of manufacture and their importance in practice are discussed. Suggestions are given for operation, firing, repairing, and preventing further damage. Refractory mortar and ramming and coating masses are fully explained with regard to their use, suitability, and proper installation. Advice for construction engineers and ordering departments for building locations and operations is given. M.V.C.

PATENTS

Electrically heating molten glass. Games Slayter (Owens-Corning Fiberglas Corp.). U. S. 2,188,927, Feb. 6, 1940 (March 3, 1933; Feb. 26, 1938).

Furnace roof construction. Hoare & Co., Ltd. (W. Davison). Brit. 516,791, Jan. 24, 1940 (July 8, 1938).

Making refractories. François Richard. U. S. 2,188,921, Feb. 6, 1940 (Feb. 17, 1936).—(1) A process of making refractories comprises crushing magnesian rock, incorporating water, calcining, crushing the calcined product, screening into fines and coarser particles, reproportioning the fines and coarser particles, incorporating water, pressing into shapes under a pressure of at least 10,000 lb. per sq. in., and curing the shapes in the presence of water. (14) A process of making refractories comprises mixing finely divided hydrateable magnesium-containing refractory material with coarser magnesium-containing refractory particles not exceeding 4-mesh, removing air by supplying through the mass water sufficient to fill the voids, introducing the wetted mass into a pressing zone and pressing into form under at least 14,000 lb. per sq. in., allowing the formed articles to set at ordinary temperatures, supplying additional moisture, and further allowing them to set.

Producing aluminum oxide from aluminiferous raw materials. A. S. Burman. U. S. 2,189,376, Feb. 6, 1940 (July 23, 1936).—A continuous cyclic process for the production of alumina from aluminiferous raw material comprises initially subjecting the raw material to decomposing exothermic reaction by contacting it with hot hydrochloric acid vapors and water to form an aluminum salt solution, insoluble residues, hydrochloric acid vapor, and steam, separating the insoluble residues from the salt solution, evaporating the solution substantially to dryness by indirect contact with hydrochloric acid vapor and steam which carries the heat evolved in the initial decomposing reaction, thermally decomposing the solid salt obtained in the evaporating step into aluminum oxide and hot hydrochloric acid and water vapors, and then utilizing the latter vapors in the initial decomposition of the raw material.

Terra Cotta

Defective tile. Onni Dahl. *Tonind.-Ztg.*, **62** [52] 565–68; [53] 576–78; [54] 586–88; [56] 607–10; [60] 648–50; [61] 659–60 (1938).—D. discusses the defects and troubles encountered in the production of unglazed tile and their probable causes and possible remedies. W.K.

Improving the appearance of clay products. H. L. Watts. *Jour. Can. Ceram. Soc.*, **8**, 50–53 (1939).—W. presents a progress report covering an investigation being carried on in the Industrial Minerals Laboratories of the Department of Mines and Resources, Canada, with the purpose of developing, from Canadian clays, engobes similar to those termed terra sigillata. These engobes are prepared by a water flotation of the superfine particles of the clay. Small quantities of various electrolytes were used. The resulting suspension was sprayed on the ware to be treated. Three clays from different parts of Canada have been investigated. Fired gloss is a function of the specific gravity of the suspension as prepared. This specific gravity is of the order of 1.10. It is believed that a surface with fairly good light-reflecting properties is obtained by applying clay particles of 1 μ or less to the ware, which tend to fill pores and interstices. These engobes have good adherence to unfired bodies and show considerable gloss before firing. They do not fuse on firing, and engobed surfaces may be fired in contact. J.G.P.

Manufacture of roofing tile. O. Schramm. *Tonind.-Ztg.*, **63** [27] 317–19; [28] 336–37 (1939).—S. discusses the steps and the problems and difficulties encountered in the manufacture of roofing tile. W.K.

Radiator casing. W. Heinze. *Gesundh.-Ing.*, **61** [22] 306 (1938).—The use of clay for the casing of radiators is emphasized. These cases are considered unique from the heating technical viewpoint. W.D.K.

Roofing tile and their manufacture. W. G. Worcester. *Jour. Can. Ceram. Soc.*, **8**, 22–28 (1939).—W. traces the development in design or pattern from the earliest known forms to modern tile. He describes the patterns generally made on this continent and points out their advantages or disadvantages. In most of the European countries soft recent clays are employed in the manufacture of roofing tile. In England and on this continent both clays and shales are used; there is a preference for the latter in the U. S. due to the demand for deep red shades and for tile of low porosity. In the forming of roofing tile, the same machines employed for stiff-mud clay products are used. W. describes the drying, setting, and firing of roofing tile. He discusses the colors usually demanded by the consumer and remarks on the possibilities offered by roofing tile to the Canadian manufacturer of clay products. J.G.P.

Salt glazing in production. Eugene C. Clemens. *Brit. Clayworker*, **48** [570] 226–29 (1939).—C. discusses the theory of salt glazing, chemical and mineral composition of the body, heat treatment required, body structure, kilns and firing, glazing materials, and glaze properties. R.A.H.

Standards for roofing tile. W. Sommer. *Tonind.-Ztg.*, **61** [100] 1108–1109 (1937).—Swiss and German standards for roofing tile are compared, especially with regard to permeability and absorption as the most important properties for a good tile roof. W.K.

Terra sigillata. A. Möser. *Tonind.-Ztg.*, **62** [2] 21–22 (1938).—Schumann's method of producing terra sigillata coatings ("Producing—," *Ceram. Abs.*, **17** [11] 358 (1938)) has several advantages, especially for terra cotta. This coating is an engobe and a glaze and it can be applied to almost every body and fired in an open fire. It is cheap, adheres well, and can be made in different colors. W.K.

Tilework in the past. Arthur Lane. *Architectural Rev.*, **85** [510] 262–65 (1939).—L. presents a historical sketch illustrated with typical examples of tilework in architectural settings. F.G.H.

Tilework today. William Tatton Brown. *Architectural Rev.*, **85** [510] 265–68 (1939).—One of the most

striking developments of modern architecture has been the use of tile. Until recently, faience and terra cotta were substitutes for masonry. Their brittle richness belied the structural story they were supposed to tell. Now they are used in a way more suited to their inherent qualities, as a tight-fitting skin neatly molded to walls and columns. The change is welcome, for the old blunt dentils and arrises which disfigured even the best terra-cotta cornice were inevitably less sharp than if they had been chiseled in marble. Tile are more suitably used as a surface covering, especially for rounded surfaces, where they can express the fact that they are formed in a mold. A curious paradox in the decay of terra-cotta ornament is noticeable in the jointing of the facing material. Previously, terra cotta was elaborately bonded to give fictitious strength to arches and columns which carried nothing, while behind, real stanchions did all the work. Now these stanchions, covered with tile, are shown on the face of the building. Tile jointing runs through; terra cotta jointing is bonded. The eye has grown so accustomed to the sham of terra cotta, that straight joints have now assumed greater structural significance. The size and disposition of the bonding are important, because tiling a surface is not so much a process of covering it with tile as covering it with joints. The tile themselves become invisible, leaving instead a network of black or white lines drawn like a veil over the surface of the building. Too many joints will look fussy; too few will spoil the scale. Tiling a surface is equivalent to underlining it. It must be worthy of emphasis and set against a contrasting material whose texture will not compete. In opposition to this conception, individual tile with small designs have been placed at random in a general tiled surface. The intention is to distract the too-critical eye from the slight imperfections of jointing which inevitably occur. The idea might be pursued further and with more conviction, covering the whole surface with elegant embossed designs. At present the surface is broken up arbitrarily at one or two points and is too reminiscent of those jazz stripes and dots which we have only just shaken off from our bathrooms and public lavatories. There need be no regret, however, that the vogue for designing tiled surfaces without any decoration or relief is short-lived, for it is almost impossible for the manufacturer to make tile which will be identical in size and shape; a certain amount of irregularity is inevitable. Glass, cork, or rubber can be cut with a far greater degree of precision and will give a more mechanically slick effect than tile or terra cotta. The comparative roughness of tile should therefore be used where it will contrast with materials capable of finer adjustment, just as bare wood looks well against polished steel. In spite of the many processes that it must go through in the course of manufacture, a good tile will always betray the source of its origin, the earth. Illustrated. F.G.H.

PATENT

Flowerpot. GUSTAF HAGLUND. U. S. 2,189,982, Feb. 13, 1940 (April 23, 1938).

Whiteware

Ceramic fixed condensers for radio transmitters. ANON. *Schriftenreihe Keram. Sondermassen, Hescho-Mitt.*, No. 18, 15 pp. (July, 1938); abstracted in *Referat. Silikatliteratur*, **5** [12] 5940 (1938).—The use of special ceramic bodies, Calit and Condensa F, in the construction of fixed condensers for transmitters is described. These materials, used as dielectrics, have a number of advantages over mica. The condensers are made in two forms, plate condensers and pot condensers, which are described. See *Ceram. Abs.*, **16** [1] 25 (1937). M.V.C.

Ceramic radio disk trimmer condensers. ANON. *Schriftenreihe Keram. Sondermassen, Hescho-Mitt.*, No. 16, 8 pp. (June, 1938); abstracted in *Referat. Silikatliteratur*, **5** [12] 5939 (1938).—The manufacture and the operation of improved ceramic plate trimmer condensers for radio receivers are described. A base made of Calite supports a rotatable disk made of Condensa C or Tempa S which is held in position by a spring. One half of the top surfaces of the base and the disk is coated with silver which is fired on. The capacity of the condenser is varied by rotating the disk through an angle of 180°. Ceramic condensers have several advantages over the usual "compression" type with mica as the dielectric. They have a rectilinear capacity curve, a smaller dispersion field, a much smaller dependence on temperature, and a greater inalterability with time because of the use of ceramic insulating materials. In these trimmer plates it is important that the metal spring serves to press the two ceramic parts together, but the amount of this pressure, which determines the capacity in compression condensers of the old type, plays only a subordinate role, and the capacity is not affected when the pressure of the spring changes. Single, double, or multiple trimmers are made. Special models with other measurements, varying initial capacity, or additional capacity are made on the same structure principle. M.V.C.

Meeting of the Whiteware Research Committee, American Ceramic Society. R. F. GELLER. *Bull. Amer. Ceram. Soc.*, **19** [2] 80–82 (1940).

Steatite masses with barium oxide content. M. OYAMA, Y. NAKAZI, AND T. NAGAMI. *Electrotech. Jour.*, **2** [1] 22 (1938); abstracted in *Referat. Silikatliteratur*, **5** [12] 5532 (1938).—Steatite, the raw material for steatite masses, yields an excellent insulation material when fired, but it is affected by moisture. The natural stone has many small cracks and cannot be cut in large pieces at the quarry. If steatite is pulverized and shaped in a press, the firing range is limited. To correct these defects, different metal oxide additions were tried. With barium oxide additions of 5 to 33.3%, calculated on the free silica, steatite masses fired from 1250° to 1400° were resistant to moisture and formed a good insulation material. M.V.C.

Technique in the industrial production of electrical insulators. MARIO D'AMBRATE. *Corriere Ceram.*, **18** [10] 337 (1937); *Bibliografia Ital.*, [II] **I** [1–3] Ingegneria Sect., Abs. 313 (1938).—The production and the different methods of manufacture of high-tension insulators are described. V.S.M.

Use of nepheline-syenite in floor-tile and wall-tile bodies. C. J. KOENIG. *Jour. Amer. Ceram. Soc.*, **23** [3] 86–91 (1940).

Use of organic dispersing agents in casting slips. IRA E. SPROAT, C. C. TREISCHEL, AND E. W. EMRICH. *Bull. Amer. Ceram. Soc.*, **19** [2] 47–58 (1940).

PATENTS

Bushing insulator. H. L. RORDEN (Ohio Brass Co.). U. S. 2,188,417, Jan. 30, 1940 (Feb. 4, 1938).

Condenser bushing. H. J. LINGAL AND E. E. ARNOLD (Westinghouse Electric & Mfg. Co.). U. S. 2,189,610, Feb. 6, 1940 (Oct. 9, 1937).

Method and apparatus for manufacturing pottery ware. W. J. MILLER. U. S. 2,187,836, Jan. 23, 1940 (Feb. 9, 1935).

Production of dielectrically high quality ceramic substances. FIDES GES. FÜR DIE VERWALTUNG UND VERWERTUNG VON GEWERBLICHEN SCHUTZRECHTEN M.B.H. Brit. 516,998, Jan. 31, 1940 (July 16, 1937).

Production of dielectrically high quality titanium dioxide. FIDES GES. FÜR DIE VERWALTUNG UND VERWERTUNG VON GEWERBLICHEN SCHUTZRECHTEN M.B.H. Brit. 516,999, Jan. 31, 1940 (July 16, 1937).

Sanitary apparatus with air gap. W. C. GROENIGER (John B. Pierce Foundation). U. S. 2,187,738, Jan. 23, 1940 (Feb. 9, 1939).

Sanitary apparatus with valved air gap. W. C. GROENIGER (John B. Pierce Foundation). U. S. 2,188,132, Jan. 23, 1940 (March 17, 1939).

Spark plug. E. R. PLUGS, LTD., AND D. A. PACY. Brit. 516,492, Jan. 17, 1940 (June 29, 1938). G. S. WEINERTH. U. S. 2,188,166, Jan. 23, 1940 (Dec. 13, 1938).

Spark plug and method of making. GEORGE MARGLIN (Aeroflex Labs., Inc.). U. S. 2,190,269, Feb. 13, 1940 (Dec. 7, 1937).

Equipment and Apparatus

Absorption and reflection measurements in the range of centimeter waves. W. KEBBEL. *Hochfrequenztech. & Elektroak.*, **53** [3] 81–89 (1939); abstracted in *Physik. Ber.*, **20** [17] 1871 (1939).—K. describes an improved optical method which can be used successfully for decimeter and centimeter waves where other methods fail; it consists in introducing frequency modulation by which the interferences between sender and receiver are eliminated. Dielectric constant and loss were determined for porcelain, fiber glass, slate, oil, and artificial dielectric materials and biological substances. High-grade insulating materials (Calite, glass) retain their good properties in this range as well as for longer waves. The measurements were made at 7.2-, 6.3-, 3.5-, and 1.65-cm. wave lengths. M.H.

Binary alloys of indium and tin. C. G. FINK, E. R. JETTE, S. KATZ, AND F. J. SCHNETTLER. *Metal Ind.* [London], **54** [18] 483–84 (1939).—The results of an investigation of the entire range of alloys of indium and tin are given. Thermal and X-ray methods were used. All the alloys were soft and ductile, with a relatively high fatigue resistance. Corrosion tests showed that the addition of either metal to the other markedly increased the corrosion resistance. H.E.S.

Centrifugal air separator. J. HEYD. *Tonind.-Ztg.*, **61** [57] 633–35 (1937).—The construction and working of a centrifugal air separator and means of varying the final product are explained. Centrifugal separators are most suitable for fine, light materials. Illustrated. W.K.

Comparative grinding tests on crystalline and amorphous quartz; grain distribution and grain forms. K. WOLF, H. HENNICKE, AND A. SMEKAL. *Z. Ver. Deut. Ing., Beiheft Verfahrenstech.*, **1939**, 115–19; *Chem. Abs.*, **34**, 3 (1940).—Crystalline and amorphous quartz under identical grinding conditions give products with identical grain-distribution curves and grain forms. Graphs, photomicrographs, and 3 references are given.

Correlated abstract of the literature for 1938 on the X-ray testing of materials. SUBCOMMITTEE IV ON CORRELATED ABSTRACTS OF COMMITTEE E-7 ON RADIOGRAPHIC TESTING. *ASTM Bull.*, No. 102, pp. 26–28 (Jan., 1940).—This committee under W. P. Davey correlates the 1938 literature on equipment for radiographic testing, equipment for testing by X-ray diffraction methods, investigations on fatigue and residual strain, precision measurement of coefficient of expansion, determination of particle size, chemical analysis by X-ray diffraction methods, and protection against hard X rays. A bibliography of books and references and a table of the lead equivalents of various materials are included. F.F.

Determination of the size of fine materials. E. SZINGER AND L. WEIL. *Tonind.-Ztg.*, **61** [51] 565–68; [52] 579–81 (1937).—A new apparatus for sedimentation analysis allows samples to be taken from the liquid column at various heights for the determination of their solid content. The particle size may vary between 10 and 60 microns. The time required for one test is about ¾ hr. W.K.

Drying by heated air. THOMAS CHESTER. *Jour. Inst. Heating & Ventilating Engrs.*, **7** [76] 161–212 (1939).—C. gives a complete description of different methods of drying, the factors influencing speed, efficiency, and economy, and its applications. He deals with evaporation in general, vacuum drying, and evaporation below the boiling point and defines dew point, absolute and relative humidity, and wet-bulb temperature. He describes the drying characteristics of materials in general, drying stages, rate of drying, effect of air velocity, air recirculation, and casehardening. Details are given on progressive tunnel, loft, compartment, cabinet, tilting tray, conveyer or chain, column, drum, cylinder surface, rotary shell, and spray driers. Drying by superheated steam and on hot floors, vapor absorption, regain of moisture, temperature and humidity control, and drying by means of conditioned air are dealt with. Fundamental laws and the more important requisites for the design of driers are given. Examples from practice are given for the drying of fish, hops, milk, paper, sugar, tea, and tobacco. A table shows regain of hygroscopic materials such as natural textile fibers, rayons, paper, and miscellaneous organic materials, these being subdivided according to origin, pretreatment, and other descriptions. Illustrated. J.M.N.

Dry-mixing method of body preparation at the plant of Smith & Stone, Ltd. E. T. MONTGOMERY. *Jour. Can. Ceram. Soc.*, **8**, 47–50 (1939).—Six bodies are produced for the manufacture of the various porcelain articles marketed. The four low-tonnage bodies are still produced by the wet method, but the two high-tonnage bodies are produced by the dry-mixing method. The installation of the dry mixing process, with auxiliary equipment, is illustrated. J.G.P.

Electrodes made of natural graphite. ERCOLE RIDONI. *Jour. Four Élec.*, **47** [9] 310–12 (1938).—R. describes the production of electrodes from natural graphite and compares them with those made from artificial graphite. The cost of raw material is higher but is more than balanced by cheaper production (in Italy). Electrical resistivity is 10 ohms/m./mm.². Oxidation in air starts at 550°C. instead of 700°C. Heat of combustion is lower with graphite from Madagascar and Ceylon, and the danger of increasing C content of metals is diminished. The average breaking strength is the same as that for artificial graphite but more uniform. The life is slightly less. They can be produced in larger sizes, even up to 2 ft. 8 in. in diameter. J.M.N.

Hardness and its determination. E. D. CONNOR. *Australasian Engr.*, **38**, 24–27, 48–50 (Sept. 7, 1938); *Jour. Iron & Steel Inst.*, **139** [1] 48A (1939).—After briefly reviewing the history of hardness testing since 1722 when Réaumur experimented with crossed 90° triangular prisms, C. discusses the factors which affect the readings obtained when measuring Brinell impressions; these factors include the deformation of the ball, the piling-up or sinking-in of the material, and the time during which the load is maintained. C. also refers to Meyer's research which has proved that, provided loading is maintained long enough for equilibrium to be reached, the following expression holds true for a given material and given ball diameter: $L = ad^n$, where L = the load in kgm., d = the diameter of the impression in mm., a = a constant, and n = a constant representing the strain hardenability. This equation is generally known as Meyer's law, and by carrying out tests at two or three different loads, a and n may be calculated. From these values a series of values for d may be calculated, and the curve of the load against the strain can thus be plotted. The Vickers hardness tester, the Firth Hardometer, the Rockwell tester, the Herbert pendulum tester, and sclerometer testers are described and compared. C. points out that while theory has not yet provided a fundamental explanation of that elusive property hardness, hardness-testing practice has supplied a means of estimating and controlling the hardness of materials with a degree of accuracy which is of the greatest benefit to industry.

Improved electric hygrometer. FRANCIS W. DUNMORE. *Jour. Research Nat. Bur. Standards*, **23** [6] 701–14 (1939); R.P. 1265. Price 5¢.—D. describes a type of electric hygrometer suitable for humidity readings which are to be recorded graphically or made at a distance remote from the point of measurement or where humidity must be determined rapidly, in confined spaces, or at low temperatures. R.A.H.

Improved technique in micropycnometric density determination. C. J. KSANDA AND H. E. MERWIN. *Amer. Mineralogist*, **24** [8] 482–84 (1939). F.J.Z.

Jeopardizing business with high mold costs. GEORGE GORTON, JR. *Ceram. Ind.*, **31** [2] 28–30 (1938).—The high initial expense for molds has been a hindrance in developing new business, but installation of the new high-speed, precision, vertical and universal milling machines has reduced this cost. The greatest reduction has been effected with mold duplicators designed similar to super-speed vertical milling machines with the addition of duplicating equipment. Mold duplicators reproduce dies or molds in exact size from actual working molds or built-up molds of brass, Bakelite, stone composition, etc. Lettering or designs on flat or uniformly curved surfaces are generally cut to best advantage with a pantograph machine, using enlarged models. E.J.V.

Measurement of average particle size by sedimentation and other physical means. PIERCE M. TRAVIS. *ASTM Bull.*, No. 102, pp. 29–32 (Jan., 1940).—T. discusses the importance of particle size below 44 microns (No. 325 sieve) as applied especially to pigments, mineral aggregates, fillers, etc., and in paper sizing materials and ceramics where a sized particle is necessary for uniform fusing. Methods used for sizing are reviewed: (1) turbidity results are not satisfactory with low-price apparatus even though a photoelectric cell is used; (2) separating and weighing methods are time-consuming; (3) microscopic methods are fair but are time-consuming and often an approximation. T. favors a sedimentation tube with which about 2500 times as much sample can be used and fairer cross section can be secured. Measurements were readily made of particle sizes from 44 microns down to 4 microns in diameter. The apparatus is based on the rate of sedimentation according to particle size of the dispersed particles in a liquid and applies to all particles larger than colloidal dimension which settle by gravity. It consists of a glass tube of 15-mm. bore and 110 cm. in fall height. There is a separate mixing chamber 15 cm. in length. At the bottom is a sedimentation-measuring tube of 7-mm. bore and 150 mm. in length graduated in millimeters and having a micrometer eyepiece. A small electric tapper keeps the sediment column level. The sample ($2^1/_2$ gm.) is mixed with a suitable liquid wetting agent, e.g., distilled water, alcohol, etc., and put in a reservoir at the top of the tube. The time required for the first particles to reach the bottom is recorded as that for the largest particles present. Agglomeration will give false readings. At regular recorded intervals the sediment is leveled off by means of the tapper, and the height of sediment is recorded by the micrometer eyepiece. The density of the liquid should be determined with a pycnometer. The settling times are based on Stokes' law of sedimentation. The radius in particle size in microns can be determined by applying the following formula derived from Stokes' equation:

$$r = \sqrt{\frac{9NV_0}{2(d_1 - d_2)g}} \times 1000,$$

where r = radius of particle in microns, N = specific viscosity of medium compared to water, V_0 = rate of sedimentation (height of fall in cm. ÷ time in sec.), d_1 = density of particle, d_2 = density of medium, and g = acceleration due to gravity (generally 980 dynes). T. presents several tests as typical runs for sulfur, barium sulfate pigment, and zinc dust. The results check with accuracy and compare favorably with those obtained with sedimentation apparatus using the microscope, a method which takes a much longer time. Five figs., one table. F.F.

Metal crystals. BRUCE CHALMERS. *Metal Ind.* [London], **53** [11] 243–46; [13] 295–98; [14] 323–25 (1938).—In metallic crystals the process of slip is believed to take place in definite directions and in fairly definite planes, with its accompanying work hardening due to the fact that any crystal has a mosaic structure, i.e., it consists of small blocks (of the order of 10^{-4} cm. in size) of perfect crystals slightly inclined to each other. The unsatisfactory state of the theory can be judged from the fact that some investigators believe the region between the mosaic blocks to be the source of weakness of crystals while others believe the existence of the mosaic structure is responsible for what strength they have. The main problem is to account for the existence of the mosaic structure and, by means of this theory or otherwise, to explain the process of glide accompanied by work hardening. The effect of temperature and impurities on the critical sheer stress required to cause glide and the conditions which determine whether glide, twinning, or cleavage takes place would probably be explained in terms of the same theory. H.E.S.

Metallurgical developments in 1938. B. W. GONSER AND A. U. SEYBOLT. *Metal Ind.* [London], **54** [2] 29–33 (1939).—Progress in metals and alloys has been rapid in the past few years due to the production of high-purity metals and to the continual efforts to develop new alloys for specific purposes and applications. Intensive research programs have been carried out by universities, individual industrial companies, and groups of industries. Research is rapidly being recognized as synonymous with progress. H.E.S.

Metallurgical progress in the clayworking industry. ANON. *Brit. Clayworker*, **48** [571] 248–49 (1939).—Among recent developments is a pug-mill knife made from nickel-chromium cast iron which is of special value in de-airing mills. It is so constructed that it prevents suction of air into the clay and leaves the steel shaft free to bend if the blade should encounter a piece of tramp iron. Excavators, power shovels, cranes, and draglines have for some time employed alloy steels to resist the effects of severe stresses and hard service. A machine designed in the form of an overhead shovel eliminates the need for the turning operation necessary in the front-end loader. The self-lubricating bearing is being applied to crushing and screening plants, excavators, etc. Fabricated chromium bearings are extremely tough and ductile and are especially suitable where toughness is a primary requirement. R.A.H.

Microscopic method of electrophoresis and its application to the study of ionogenic and non-ionogenic surfaces. H. A. ABRAMSON. *Trans. Faraday Soc.*, **36** [1] 5–15 (1940).—A. discusses various types of cells to be used in making quantitative measurements of the electrical mobility of microscopically visible particles. G.R.S.

Photoelectric null indicator for matching light intensities. M. KNIAZUK. *Jour. Optical Soc. Amer.*, **29**, 223–25 (1939).—To adapt existing visual-observation instruments to the photoelectric type, an electronic null indicator has been developed which uses standard radio parts. The condition of balance is observed upon a cathode ray tube, and the proper adjustments are performed manually. When used with a spectrophotometer, this electronic apparatus extends readings further into the red than can be observed visually. A.P.

Potentiometric method for the accurate measurement of hydrogen-ion activity. WALTER J. HAMER AND S. F. ACREE. *Jour. Research Nat. Bur. Standards*, **23** [6] 647–62 (1939); R.P. 1261. Price 5¢.—A potentiometric method for measurements of hydrogen-ion activities in aqueous solutions is described. Galvanic cells without liquid junctions are used. The hydrogen-ion activity may be calculated from the electromotive force by thermodynamic methods, using the Nernst equation, in which the concepts of activity and interionic attraction are incorporated. R.A.H.

Preparation of cross-breaking bars by mechanical shaking. R. GRÜN. *Tonind.-Ztg.*, **61** [68] 749–51 (1937).—G. describes apparatus for making cross-breaking bars by mechanical shaking instead of by stamping. Comparative tests show that the new method gives uniform results and the same rating for the cements. The figures are higher for strength and lower for shrinkage. Shaking is faster and more uniform. W.K.

Psychrometric chart; application and theory: VI. WILLIAM GOODMAN. *Heating, Piping & Air Conditioning,*

11 [11] 671–74 (1939).—G. considers fogged air and calculations from the chart involving this condition. Six figs., one numerical example. For Part IV see *Ceram. Abs.*, **19** [2] 50 (1940). J.L.G.

Re-examination of the correction curve of the X-ray camera used for the powder method. S. KOZU, K. OMORI, AND T. TAKEUTI. *Jour. Japan. Assn. Mineralogists, Petrologists, & Econ. Geologists*, **23** [1] 1–18 (1940).—The authors studied the correction curve used for the powder X-ray method. They discuss the following items as the main sources of errata: (1) inaccurate centering, (2) elongation and shrinkage of film by development, (3) effect of diameter of sample rod, (4) fineness of the powder, (5) effect of temperature, (6) shape of the camera, (7) incorrect setting of film to the camera, and (8) incorrect measurement of the distance of lines. They determined the lattice constant with an accuracy of within 0.001 a.u. Y.K.

Sensitive optical strain gauge. S. C. REDSHAW. *Jour. Sci. Instruments*, **16** [5] 150–55 (1939).—A strain gauge capable of measuring positive and negative strains to about 1.0×10^{-6} on a gauge length of 3 or 4 in. has a linear calibration over a strain range of at least 500×10^{-6}. It could be modified to operate on other gauge lengths. Although designed for the measurement of strains in masonry and metal bridges, it could be used for other structural experimental work. The design provides that the motion between a fixed and a movable knife-edge will rotate a flexure pivot, the light from a target being reflected by a mirror mounted on the torque bar of the flexure pivot into a microscope unit set in the cover of the gauge. The microscope unit is fitted with a screw micrometer eyepiece. When the flexure pivot is operated by a change in the strain of the test specimen to which the gauge is attached, the position of the image of the target produced in the eyepiece is altered, the change being recorded by means of the micrometer wheel of the eyepiece. Construction, adjustments, attachment, operation, sensitivity, and calibration are discussed in detail. Three figures. J.L.G.

Simple refractometer. F. BENFORD. *Jour. Optical Soc. Amer.*, **29**, 352–54 (1939).—A prism-shaped specimen holder is mounted on a comparator table. Determinations of the refractive index of glass to the second decimal place are derived graphically from measurements of sample thickness and image displacement. A.P.

Torsion microbalance for determining specific gravities of minerals. HARRY BERMAN. *Amer. Mineralogist*, **24** [7] 434–40 (1939). F.J.Z.

Use of air-velocity meters. G. L. TUVE, D. K. WRIGHT, AND L. J. SEIGEL. *Heating, Piping & Air Conditioning*, **11** [11] 703–708 (1939).—The calibration and use of air-velocity meters are considered. 13 figs., 4 tables. J.L.G.

SEPARATE PUBLICATION

Procedure for Applying for Tests Made on All Explosives and Blasting Devices by the Explosives Division of the Bureau of Mines. ANON. *U. S. Bur. Mines Schedule*, 1 C. Supt. of Documents, Govt. Printing Office, Washington, D. C. Price 5¢. R.A.H.

PATENTS

Apparatus for measuring humidity. R. M. BUFFINGTON AND G. K. ASHBY (Servel, Inc.). U. S. 2,189,855, Feb. 13, 1940 (April 26, 1937).

Apparatus for projection of molten pulverized bodies. F. P. C. BENOIT. U. S. 2,190,326, Feb. 13, 1940 (July 15, 1936).—A spray gun for melting powder and spraying the resulting molten matter in an atomized state.

Core structure for clay extruding dies. E. H. PETTLER. U. S. 2,188,984, Feb. 6, 1940 (Dec. 2, 1938).

Dynamically compensated strain gauge. W. M. BLEAKNEY. U. S. 2,189,775, Feb. 13, 1940 (Dec. 12, 1936).

Machine for grinding the edges of tile, etc. BRITISH & INTERNATIONAL FLOORING CO., LTD. (K. F. Goetzl). Brit. 517,141, Jan. 31, 1940 (July 19, 1938).

Machine for grinding the surfaces of tile, etc. BRITISH & INTERNATIONAL FLOORING CO., LTD. (K. F. Goetzl). Brit. 517,140, Jan. 31, 1940 (July 19, 1938).

Press tools for the production of dust-pressed tile, etc. G. WRIGHT AND B. ADAMS (trading as Potteries Ventilating & Heating Co.). Brit. 516,625, Jan. 17, 1940 (June 30, 1938).

Psychrometric apparatus for direct reading of humidity. JULES CRAPEZ. U. S. 2,189,857, Feb. 13, 1940 (July 8, 1937).

Pyrometer tube. C. E. NOBLE (Claud T. Gordon Co.). U. S. 2,187,949, Jan. 23, 1940 (Dec. 22, 1937).—A pyrometer protecting tube composed of alloy steel containing 27 to 35% chromium, the tube having an outer layer substantially impervious to gases comprising a coating of approximately pure chromium.

Kilns, Furnaces, Fuels, and Combustion

Firing with double grate. RICHARD ALDINGER. *Glashütte*, **69** [26] 449–52 (1939).—The process was studied in detail to determine how maximal increase in production with this type of firing could be obtained. For best results it is necessary to use a modern furnace which furnishes the extra heat necessary for firing with a double grate. A longer firing time should be made possible by organizing operation so that larger charges of the same type of piece can be fired. The advantage of double-grate firing becomes less important the longer the firing time is in proportion to the time of loading and unloading of the grate. If the firing time is long (over 5 to 6 min.), the increased production achieved by the double grate is nullified because the grate outside the furnace cools too much, which prolongs firing time. M.V.C.

Firing zone in circular kiln. R. CLAUSS. *Tonind.-Ztg.*, **63** [1] 7–8 (1939).—A long firing zone and larger charges of fuel at longer intervals result in a longer, more penetrating flame, a more even distribution of heat, and an easier regulation of the firing. This applies to kilns of both small and large cross section. Automatic stokers can be adapted to this method of firing. W.K.

Four-degree spread at 2400°F. ANON. *Ceram. Ind.*, **34** [2] 46–48 (1940).—A production-size kiln at the Globe-Union Co. plant is operated continuously at 2400°F., and ware temperature is held within 4°F. The new kiln is used for firing small ceramic condenser bodies averaging about $1^3/_4$ in. in length and $^1/_4$ in. in diameter. Bodies are placed on end in square and diamond-shaped saggers which move through the kiln at a rate of 3 to 4 in. per min. The high-temperature zone of the kiln is 45 in. long. The main kiln housing is 10 ft. 7 in. and includes three distinct temperature zones: (1) 1000° to 1600°F., (2) 1600° to 1950°F., and (3) 1950° to 2500°F. Heat is supplied by electricity, nickel-chromium resistor elements being used in zone 1, Alloy 10 elements in zone 2, and 10 Globar heating elements in zone 3. A total of 250 kw.-hr. is required to bring the kiln to 2400°F.; 44 kw. are required to operate the kiln with full ware load. A gas-fired kiln of the same output would use 1000 to 1300 cu. ft. of 550 B.t.u. gas per hr. Because of the nature of the ware, it is essential that an oxidizing atmosphere be maintained. This is easily done with electric heat. By placing the heating elements in such a way that radiated heat from the side walls and roof is focused directly on the line of saggers, a uniform high heat is maintained and no hot spots are developed. Close control is maintained by two sensitive heat detectors in the roof of the kiln. These consist of a spider-web structure of thermocouple wires with a common junction in the center. Heat is

focused on this junction by a glass lens, much in the same way a burning glass is used to focus the sun's rays. The temperature of the lens is kept to about 110°F. by means of a cooling water jacket. In the electric kiln, no blast action of flame is encountered, and therefore insulating refractories are used throughout: semi-insulating in zone 1, full insulating in zone 2, and refractory insulation in zone 3. The brick have no mechanical load to bear, as the walls are built up inside a load-bearing steel shell. Illustrated. L.M.C.

Remote gas supply for ceramics. F. DIETRICH. *Gas- & Wasserfach*, **82** [30] 545–48 (1939).—D. discusses the question (especially important in Germany) of saving coal by supplying energy in the form of gas over long distances and how the ceramic industry can use gas for drying and particularly for firing, glazing, and decorative firing. The various processes and batch and continuous furnaces are considered, and coal and gas firing are compared. To use gas with advantage, the furnace should be designed for gas firing; changing from coal to gas is not efficient. Such design should take into account proper hearth cars and conveyers, the smallest possible hearth area, fast progress of ware through the furnace, overpressure in the furnace instead of underpressure, and small furnace cross section in order to eliminate differences in furnace temperature and atmosphere over the the section. The following fuel consumption figures for tunnel kilns are given:

Material	Temp. (°C.)	Coal (kgm./m.³)	Coal (kgm./kgm. ware)	Pure gas (m.³/m.³)	Gas (m.³/kgm. ware)	Kw.-hr./ kgm. ware	Time for firing and cooling (hr.)
Porcelain ware	1410	100–120	1.43 –1.71	140–170	2.0 –2.42	2.5 –4.5	28– 40
Electrical porcelain insulators	1410	100–125	0.95 –1.25	125–156	1.20 –1.56	2.2 –4.0	90–100
Earthenware (crude)	1280	50– 56	0.20 –0.23	65– 75	0.27 –0.31	1.10–1.40	27– 37
Earthenware (smooth)	1150	45– 50	0.30 –0.34	60– 80	0.40 –0.53	1.0 –1.30	17– 30
Sanitary earthenware (crude)	1280	38– 48	0.49 –0.62	50– 64	0.64 –0.82	1.60–1.80	34– 50
Sanitary earthenware (smooth)	1100	32– 40	0.50 –0.63	43– 56	0.67 –0.88	1.30–1.60	23– 36
Tile (crude)	1280	80– 95	0.12 –0.27	110–126	0.22 –0.45	0.50–0.75	80–100
Tile (smooth)	1060	70– 85	0.24 –0.35	93–114	0.40 –0.60	0.40–0.60	30– 50
Floor plates	1280	110–130	0.375–0.37	147–170	0.42 –0.50	0.50–0.75	100–120
Fire clays	1300	80–100	0.08 –0.10	107–130	0.107–0.13	0.55–0.80	70– 90

Coal and gas consumption is referred to a 1-m.³ combustion chamber. D. describes a new furnace 50 m. in length which uses only 11.5 m.³ gas per 1 m.² car surface with 10 kgm. porcelain at 1410°C., i.e., 1.15 m.³ gas per 1 kgm. porcelain. M.H.

Fundamental principles of gas-producer control. J. G. BENNETT. *Jour. Soc. Glass Tech.*, **23** [97] 154–70T (1939).—The variable factors in gas-producer operation are enumerated and discussed. For the automatic control of a gas producer it is desirable to have a potentiometer recording controller for controlling the coal feed and gas temperature, a pressure recording controller to control gas pressure or blast volume, and a vapor pressure bulb recording controller to control blast saturation temperature. The operation of such devices is described. A study was made of the influence of the fuel bed on producer control. Local variations of the porosity of the fuel bed between 30% and 50% result in corresponding variations in velocity up to 2.5:1, while variations in particle size between 1 and 2 lead to a change in velocity of 1.4:1. Experiments were carried out on an 8-ft. Wellman producer comprising a study of the over-all pressure drop with different sizes of fuel and thickness of fuel bed and the exit velocity of the gas from the top of the fuel bed, employing a Pitot tube measuring velocities of about 1 ft. per sec. and later a Velometer measuring up to 0.5 ft. per sec. G.R.S.

Gas-fired furnaces. A. G. ROBIETTE. *Metal Ind.* [London], **55** [17] 365–68 (1939).—Advances in gas-furnace technology in the past five years have led to a great increase in efficiency and flexibility. This has broadened the use of gas heating for purposes which were previously open only to electric furnaces. This advancement has been brought about by a more liberal application of insulation, improvements in burner design, and the use of radiant and recuperative alloy tubes as well as heat-resisting alloys. Other improvements have been effected by the use of refractory radiant blocks, gas-mixing devices, good atmosphere control, and convection heating where low temperature and uniformity is desired. H.E.S.

BOOK AND SEPARATE PUBLICATION

Nature and Origin of Coal and Coal Seams. A. RAISTRICK AND C. E. MARSHALL. English Universities Press, London, 1939. 282 pp. Price 12s 6d. Reviewed in *Geographical Jour.*, **94** [5] 425 (1939). F.G.H.

Wellman-Galusha Gas Producer. WELLMAN SMITH OWEN ENGINEERING CORP., LTD. Reviewed in *Brit. Steelmaker*, **6** [1] 19 (1940).—Details of the Wellman-Galusha gas producer are given. It is claimed to be particularly suitable for the production of gas from low-grade fuels. R.H.

PATENTS

Manufacture of silicon carbide resistors. A. J. THOMPSON (Carborundum Co.). U. S. 2,188,693, Jan. 30, 1940 (July 26, 1938).—A method of recrystallizing a silicon carbide resistor in order to produce a resistor having relatively low resistance at room temperature comprises forming a resistor element from a mix consisting principally of silicon carbide grains and a temporary binder and subjecting the formed resistor, while protected from oxidation, within the highly heated walls of a kiln, furnace, etc., to a temperature of at least 2200°C. for a period not exceeding 30 min.

Production of combustible gases from bituminous fuels. WALTER MALKOMES (Koppers Co.). U. S. 2,190,293, Feb. 13, 1940 (Nov. 11, 1936).

Resistor and method of making. E. R. STOEKLE AND G. M. EHLERS (Globe-Union, Inc.). U. S. 2,188,667, Jan. 30, 1940 (Jan. 8, 1935).—A method of making an electrical resistor comprises mixing with a fine-grained plastic ceramic a portion of a compound convertible by heat into an electrical conductor, adding to the mixture a coarse-grained refractory ceramic, mixing the whole into a uniform plastic mass, extruding the mass into rods, drying the rods, and firing them at the maturing temperature of the ceramic mixture.

Geology

Absolute value of the principal piezoelectric modulus of quartz. A. LANGEVIN. *Compt. Rend.*, **209** [17] 627–30 (1939).—The widely differing values of the piezoelectric constant of quartz are, after thorough investigation, ascribed to the overlooking of defects in the optical axes. By applying a method which cuts entirely pure, optically correct lamellas from quartz, the value of the modulus is determined to slightly more than 7×10^{-8} c.g.s.;

the piezoelectric modulus can be considered as a true physical constant of quartz. Redeterminations by other methods confirmed the result. M.H.

"Amphoteric" double layer and the double ionic exchange in soils. SANTE MATTSON AND LAMBERT WIKLANDER. *Trans. Faraday Soc.*, **36** [1] 306–19 (1940).—It has been pointed out that it would be theoretically possible to remove all the anions and cations from a solution by passing it through alternate layers, or a coarse mixture, of acidoids and basoids. The Donnan distribution of ions in the soil has many important consequences, e.g., the effect of a concentration and a dilution of the soil solution on the mobility of the monovalent and divalent ions. A dilution favors the entrance (in the soil complex) of the divalent ions and the exit (in the soil solution) of the monovalent ions. A concentration reverses the process. It might be said that the soil complex "inhales" divalent ions and "exhales" monovalent ions upon wetting and "inhales" monovalent ions and "exhales" divalent ions upon drying. Since a leached soil means a dilute soil solution, it can be readily understood why, in the humid soils, the divalent base-forming cations are present in the exchange complex in a greater proportion than in the original silicate rocks and in the soil solution. The simultaneous exchange of anions and cations at the equi-ionic point of soils takes place according to the mass law as expressed by the Donnan equilibrium. The valence effect expresses itself in the form of maxima in exchange acidity and exchange alkalinity in dilute solutions. The double ionic exchange has led to the conception of an amphoteric electrical double layer. G.R.S.

Aplite, a new ceramic material. P. S. DEAR AND J. W. WHITTEMORE. *Jour. Amer. Ceram. Soc.*, **23** [3] 77–80 (1940).

California potters use local china clays. HOWARD R. ERWIN. *Ceram. Ind.*, **34** [2] 56–58 (1940).—Pottery manufacturers in Calif. have recently incorporated local china clays into their regular bodies. One of the clay deposits, located in Orange County, gives a product similar to the English china clay known as VC No. 1. As it comes from the pit, the material is 40% china clay and 60% silica. The silica is separated by water flotation and is used in the pottery and foundry industries. Drying and shrinkage properties of the clay are close to those of the English clay, and it has about the same plasticity and water of plasticity. California clay has a slightly higher absorption and greater refractoriness, which are probably accounted for by a slightly higher alumina content and a lower alkaline content. L.M.C.

Correlation of quartz deformation with its crystal structure. H. W. FAIRBAIRN. *Amer. Mineralogist*, **24** [6] 351–68 (1939).—Although it is well known that the manner in which a crystal deforms is governed by its structure, few correlations have been made. F. gives the results of an analysis of this type for quartz and summarizes them in tabular form. F.J.Z.

Davoli's quartz deposits for the manufacture of colorless glass. RENATO MORETTI. *Corriere Ceram.*, **18** [10] 313 (1937); *Bibliografia Ital.*, [II] **I** [1–3] Ingegneria Sect., Abs. 315 (1938).—Davoli's quartz deposits are described. The chemical and screen analyses show that this material entirely fulfills the specifications for making the best colorless and optical glasses. V.S.M.

Deposition of oxide coatings by cataphoresis. M. BENJAMIN AND A. B. OSBORN. *Trans. Faraday Soc.*, **36** [1] 287–95 (1940).—The production of noncolloidal cataphoretic suspensions of alkaline-earth carbonates and alumina is described. The carbonate particles appear to be both negatively and positively charged. Immediately after switching on the current, a heavy deposit can be obtained on the anode, but subsequent deposition occurs almost exclusively on the cathode. Alumina, having a dielectric constant similar to that of the carbonates, follows Coehn's rule, being deposited on the anode. The authors believe that insulating materials can be deposited cataphoretically from noncolloidal suspensions. G.R.S.

Differential thermal analysis of kaolinite. S. CAILLÈRE AND S. HÉNIN. *Compt. Rend.*, **209** [19] 684–86 (1939).—The authors show the manner in which the previously found exothermic phenomenon at about 1000°C. (by which the content of kaolinite in a mixture of clays can be determined) is changed and influenced by Na ions, particle size, and fixed metal and the manner in which the metal is fixed. The shape of the curve obtained by the differential thermal analysis with the Saladin-Le Châtelier apparatus shows these influences clearly; they are explained in detail. M.H.

Fractionation of nonplastic powders by sedimentation in water. STANLEY E. LULL AND A. S. WATTS. *Bull. Amer. Ceram. Soc.*, **19** [2] 68–70 (1940).

Giving clay the third degree: I. T. W. GARVE. *Brick & Clay Record*, **96** [2] 15–17 (1940).—G. describes, in the examination of clay, its preparation, water of plasticity, wet strength, lamination, dry strength (formula given), and moduli of rupture. Illustrated. T.W.G.

Mechanism of dolomitization of calcareous sediments. A. RIVIÈRE. *Compt. Rend.*, **209** [19] 691–92 (1939).—R. develops a new theory in explanation of the transformation of calcareous deposits by sea water into dolomite. According to this theory, transformation can take place only in fairly stagnant regions where the water of impregnation circulates slowly and is renewed only slightly or not at all. The conditions are explained in detail. M.H.

Metamorphic rocks (sakenites) contained in the crystalline schists of southern Madagascar. A. LACROIX. *Compt. Rend.*, **209** [17] 609–12 (1939).—The name "sakenite" is a collective definition of paragneiss rich in sillimanite, cordierite, and almandine and associated with pyroxenites and amphibolites. The sakenites (named after the district of Sakeny, Madagascar) are sugar-white rocks, of which four principal types are distinguished. The characteristics of the types are discussed at length. M.H.

Neogenesis of minerals in the interior of rocks by heating in gas or water vapor under high pressures. Production of artificial metamorphism phenomena. A. MICHEL-LÉVY AND J. WYART. *Compt. Rend.*, **209** [3] 175–77 (1939).—Experiments on the artificial synthesis of minerals by producing, in an explosion bomb, a pressure of 3000 to 4000 kgm. per cm.^{2} and a temperature of 500° to 600°C. and maintaining them for about 10 hr. show that gases under high pressures can easily penetrate into the core of a rock. If the rock is crystalline the gases penetrate by all the joints and interstices; if the rock is of fine elements rich in colloidal matter, they penetrate by general absorption (imbibition). This leads easily to artificially produced crystallization and metamorphosis in the rock, a theory which is applied to explain the character of preexisting rocks. M.H.

Origin of igneous rocks and their mineral constituents. J. F. SCHAIRER. *Sci. Monthly*, **49** [2] 142–54 (1939).—The general processes operating in nature to produce the great diversity of igneous rocks are described. The broader problem of the chemistry of igneous rocks is shown to concern only ten rock-forming chemical substances. The laboratory technique of studying the temperatures and processes of rock formation is illustrated and described. Each mineral system studied yields information concerning certain rock formations and enables some minerals to be used as geological thermometers. H.E.S.

Origin and utilization of diatomaceous peat deposits. PAUL S. CONGER. *Sci. Monthly*, **49** [6] 509–23 (1939).—C. describes the origin and recovery of diatomaceous peat deposits of northern Wisconsin lakes. The muck is dug from shallow marshy bogs either by hand or by dragging or pumping. It is hauled to a plant where the excess water is removed by pressing and the organic matter is removed by burning in incinerators, leaving only the pure diatoms as a white cake. Similar operations are carried out in Florida, New York, and New Hampshire. Although very pure fossilized diatomaceous earth deposits occur throughout the western part of the country, the peat deposits of the east are of greater accessibility to eastern industrial markets and possess superior qualities for industrial purposes. Illustrated. H.E.S.

Properties of clays in graphs. K. SPINGLER. *Tonind.-Ztg.*, **61** [101] 1115–19 (1937).—S. describes and recommends the use of graphs in presenting the properties of clays, such as shrinkage and absorption in relation to temperature. W.K.

Purification of the Kur'ino refractory clays. A. A. SHRADER. *Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Mineral. Syr'ya*, No. 127, pp. 82–99 (1938); *Chem. Abs.*, **33**, 7977 (1939).—Purification of the Kur'ino clays (in the Urals) is complicated by the presence of one or more of the following admixtures: quartz, spherosiderite, pyrite, and marcasite. Preliminary laboratory experiments included (1) wet purification with the use of electrolytes, (2) air separation, (3) flotation, and (4) magnetic separation on a Johnson induction separator. Methods 1 and 2 proved best. The electrolytic method yielded a product containing much H_2O so that a combined method was adopted which consisted of air separation in three stages followed by electrolytic purification of the coarse fraction. The ceramic properties of the purified products were quite satisfactory.

Quarrying marble in northwest Greenland. O. EKLUND. *Tek. Tid.*, **70C** [2] 5–7 (1940). R.A.R.

Use of nepheline-syenite in heavy clay products. J. H. CHILCOTE AND C. J. KOENIG. *Jour. Can. Ceram. Soc.*, **8**, 53–58 (1939).—The authors give the results obtained in an investigation to determine the influence of small additions of nepheline-syenite and combinations of nepheline-syenite with dolomite on the physical properties of fire clay and shale brick. The addition of nepheline-syenite in small amounts to fire clays and shales lowers the absorption and increases the firing shrinkage and mechanical strength. Some fluxing action was noticed as low as cone 09. Nepheline-syenite also matures the bodies at lower temperatures, which offers an economy in fuel. J.G.P.

Chemistry and Physics

Accuracy requirements in fifth place refractometry. H. W. STRAAT AND J. W. FORREST. *Jour. Optical Soc. Amer.*, **29**, 240–47 (1939).—The requirements that must be met to extend the reading accuracy of the Abbe refractometer to a probable error not exceeding two or three units in the fifth decimal place are analyzed under the following topics: refractometer prism's index and angle, compensating prism, observing telescope, and the bearing about which the prism and scale rotate. A.P.

Calculating the optical constants from reflection coefficients. R. TOUSEY. *Jour. Optical Soc. Amer.*, **29**, 235–39 (1939).—A graphical method has been developed for the determination of refractive indices and extinction coefficients from reflecting power data. A.P.

Detection of titanium ion. O. K. DOBROLYUBSKIĬ. *Zhur. Priklad. Khim.*, **11**, 123–25 (1938).—A modification of the Knecht reaction has been developed. Ti salts are dissolved in 6 *N* HCl, and the solution is colored blue by 3 to 4 drops of 0.025% methylene blue. A piece of granulated zinc is added, and the solution decolorizes, the speed depending on the amount of Ti present. P.B. & E.S.

Determining calcium by the adsorption titration method. N. A. FREZE. *Zhur. Priklad. Khim.*, **12**, 949–50 (1939).—F. found that hematein and hematiline are adsorption indicators for volumetric determinations of calcium by sodium oxalate. A rapid method of determining calcium in the glass batch has been developed. P.B. & E.S.

Direct optical measurement of individual principal stresses. J. H. A. BRAHTZ AND J. E. SOEHRENS. *Jour. Applied Physics*, **10**, 242–47 (1939). A.P.

Equilibrium phases of the system $CaO \cdot Cr_2O_3$–$CaO \cdot Al_2O_3$. F. I. VASENIN. *Zhur. Priklad. Khim.*, **12**, 651–54 (1939).—Several solid solutions are formed. The fusibility curve is smooth, without minimum and maximum points. P.B. & E.S.

Formation of deposit by electrophoresis. H. C. HAMAKER. *Trans. Faraday Soc.*, **36** [1] 279–87 (1940).—From suspensions of $BaCO_3$, $BaSr(CO_3)_2$, a mixed crystal (1:1) of $BaCO_3$ and $SrCO_3$, MgO, $MgCO_3$, Al_2O_3, and CaF_2 in certain organic media, it is possible to apply a coating of the suspended material by electrophoresis. The experimental aspects of this phenomenon were investigated. Within certain limits, the amount deposited is proportional to the time, the surface of the electrode, the electric field, and the concentration. H. describes a simple method for studying the density of the layers and results obtained with it. G.R.S.

Formation of strontium aluminates from oxides in the solid state. W. JANDER AND A. KRIEGER. *Z. Anorg. & Allgem. Chem.*, **235** [1–2] 89–95 (1937).—Al_2O_3 and SrO form four compounds: $3SrO \cdot Al_2O_3$, $SrO \cdot Al_2O_3$, $SrO \cdot 2Al_2O_3$, and $3SrO \cdot 16Al_2O_3$. X-ray spectrometry shows that $SrO \cdot Al_2O_3$ is always the primary product when the components are heated together in the solid state, no matter in what proportions the components are present. From this compound $3SrO \cdot Al_2O_3$ results without difficulty; the other two compounds are not formed under the conditions of the experiment. W.K.

Fusion-point diagrams of highly refractory oxides: VIII, Systems with CeO_2. H. v. WARTENBERG AND K. ECKHARDT. *Z. Anorg. & Allgem. Chem.*, **232** [2] 179–87 (1937).—The fusion points of CeO_2 with BeO, CaO, MgO, Al_2O_3, TiO_2, ThO_2, Fe_2O_3, Mn_2O_3, and Cr_2O_3 and of MgO–La_2O_3 and ZrO_2–La_2O_3 are presented in diagrams. All mixtures gave simple solutions with the exception of Cr_2O_3 which forms a compound, $CeCrO_3$. When fused in mixtures, CeO_2 is reduced to Ce_2O_3; when heated by itself it is stable and unfusible up to 2600°C. Together with ThO_2 it is the most refractory oxide. The melting point of Cr_2O_3 was established as 2435°C. For Part VII see *Ceram. Abs.*, **16** [10] 313 (1937). W.K.

Improved calculator for obtaining tristimulus values from spectrophotometric curves. F. W. SEARS. *Jour. Optical Soc. Amer.*, **29**, 77–78 (1939).—A simply constructed instrument calculates tristimulus values by the method of selected ordinates. A.P.

Influence of particle size on the physical behavior of colloidal systems. H. C. HAMAKER. *Trans. Faraday Soc.*, **36** [1] 186–92 (1940).—It is generally assumed that the difference between suspensions and colloidal solutions is only a difference in particle size; the size of the particles, however, is an important factor, as many properties of a sol depend on the ratio of forces of different origin which act on the particles. Each force varies in its own way so that the ratios may be influenced greatly by particle size. The forces which may play a part and their dependence on particle size are discussed. On the basis of this analysis, the behavior of colloidal systems under gravity or in a centrifuge is discussed. H. specially suggests that observations on the properties of a deposit obtained by centrifuging may provide valuable information concerning the shape of the potential curves valid in the sol. Literature dealing with similar problems is discussed. G.R.S.

Influence of transition points upon speed of formation of the cobalt spinel from oxides in the solid state. J. A. HEDVALL AND L. LEFFLER. *Z. Anorg. & Allgem. Chem.*, **234** [3] 235–36 (1937).—The reactions $CoO + Al_2O_3 = CoO \cdot Al_2O_3$ and $Co_2O_3 + 3Al_2O_3 = 3(CoO \cdot Al_2O_3) + {}^1/_2O_2$ were studied. Al_2O_3 was produced by igniting $Al(OH)_3$ at 800°C. At this temperature Al_2O_3 is in a state of transition to γ-Al_2O_3. The mixture of the oxides was heated in a stream of nitrogen for 5 and 15 min. The results are presented in graphs. The influence of the temperature of the transition of γ- to α-Al_2O_3 and of Co_2O_3 to CoO upon the rate of reaction is clearly visible. Dead-burned corundum (α-Al_2O_3) reacts but slowly. W.K.

Isopachic stress patterns. M. M. FROCHT. *Jour. Applied Physics*, **10**, 248–57 1939).—Isopachic (equal thickness) stress patterns give the loci of equal sums of principal stresses as distinguished from the loci of equal

differences given by photoelastic patterns. At present they are mainly of scientific interest, since they complete the optical solution of two-dimensional stress problems, thereby eliminating the need for point-by-point exploration of the $(p + q)$ values. They can be obtained directly from opaque models and may prove useful in the study of surface stresses on actual structures in service. The methods, theory, and some results obtained with this new technique are briefly discussed. A.P.

On what does the beginning of flow and ultimate strength of a material depend? O. Föppl. *Mitt. Wöhler-Inst. Braunschweig*, No. 35, pp. 56–70 (1939); abstracted in *Physik. Ber.*, **20** [18] 1935–36 (1939).—Discussing the fact that each triaxial state of stress can be decomposed into two states of stress, viz., one which depends only on the elasticity modulus for general normal stress and one which depends only on an elasticity constant for stresses without change of volume, F. concludes that neither flow limit nor ultimate strength is exceeded if only the former state of stress occurs, as both beginning of flow and ultimate strength depend mainly on the largest shearing stress. The mechanical strength of a material depends on the magnitude of the second state of stress. M.H.

Photoelastic method of stress analysis. R. D. Mindlin. *Jour. Applied Physics*, **10**, 273–94 (1939); see *Ceram. Abs.*, **18** [10] 276 (1939). A.P.

Physical chemistry of interfacial reactions. E. Wicke. *Z. Ver. Deut. Ing., Beiheft Verfahrenstech.*, **1939**, 127–30; *Chem. Abs.*, **34**, 18 (1940).—W. discusses the following subjects: adsorption, kinetic processes at the interface, importance of the interface in reactions of solids, catalysis, and energy exchange at the interface.

Qualitative determination of fluorine in minerals. Frank C. Foley and Philip W. West. *Amer. Mineralogist*, **24** [6] 398–99 (1939).—A method for the quantitative determination of fluorine in samples of ground water from North Dakota which proved reliable for amounts of less than 1 p.p.m. of fluorine has also been used successfully for the qualitative determination of fluorine in minerals. The procedure is a modification of the zirconium-alizarin colorimetric determination of fluorine in water and depends on the fading of a zirconium-alizarin lake in the presence of fluorine. The pink color fades to yellow, the amount and speed of fading being in direct proportion to the fluorine present. F.J.Z.

Radiation properties of different substances in the temperature range 250° to 800°C. M. Pirani. *Jour. Sci. Instruments*, **16** [12] 372–78 (1939).—P. presents a simple method for the comparison of the total radiation from sample plates. Quartz glass is used as the reference plate. The plate to be measured is placed in a uniformly heated chamber until it has acquired the temperature of the chamber. It is quickly withdrawn to a position opposite a thermopile (connected to a galvanometer). A constant solid angle of radiation is cut out by diaphragms, the radiation being mainly measured perpendicular to the radiation surface. A correction is applied for the heat loss during the withdrawal period and for the different time lags due to the measuring device. By this method the total radiation of the sample can be compared with the radiation of the standard at any temperature. Curves obtained for the relative emissivity (black body = 100) by this method are given for quartz glass (calculated and by experiment), opaque quartz, platinum foil (on quartz), thorium oxide, aluminum oxide, zirconium silicate, silicon carbide + 25% ball clay, magnesium oxide, Osira glass HZ6X, Pyrex brand glass, L_1 lead glass, X_7 soda glass, HH glass, ball clay 60/40, ball clay 4, and graphite. The setup and operation are described in detail. Seven figs. J.L.G.

Reactions in the solid state between synthetic and mineral chromite of iron and carbonate and oxide of magnesium. J. A. Hedvall and V. Ny. *Z. Anorg. & Allgem. Chem.*, **235** [1–2] 148–52 (1937).—The reaction $MgO + FeO \cdot Cr_2O_3 = MgO \cdot Cr_2O_3 + FeO$ was investigated, using artificial and mineral iron chromite and magnesium carbonate and magnesium oxide. The reaction proceeds faster and at a lower temperature with the synthetic product. At 900°C. the reaction is completed to about 60%. The size of the material is important. It should be finer than the 6400-mesh per cm.² sieve. $MgCO_3$ acts at a temperature 100° to 150° lower due to the nascent state of the oxide. W.K.

Repulsive forces between charged colloid particles and the theory of slow coagulation and stability of lyophobe sols. B. Derjaguin. *Trans. Faraday Soc.*, **36** [1] 203–15 (1940).—A general expression for the free energy of charged conductors in electrolytes is given. A method for measuring the forces of repulsion (pressure) exerted by thin polymolecular liquid films is described. The data obtained in this way show, for glass and other hydrophile surfaces, great deviations with theory based on the equation of Debye-Huckel at average and high concentrations, which points to the presence of a nonelectrostatic mechanism of this effect. For the majority of liquids investigated, the pressure of a thin film decreases to zero only when its thickness is of the order of 0.2 to 0.3μ, which points to the comparatively large radius of action of surfaces upon the neighboring liquid layers. D. gives proof that the forces responsible for these effects are neither of the nature of Van der Waals' forces nor of the nature of dipole forces. The pressure of thin layers of liquids depends to a great extent upon the concentration of dissolved molecules, including nonelectrolytes also, and this may be connected with the diffuseness of adsorption layers in nonelectrolytic solutions as well. This effect may be used to explain the mechanism of the stabilizing action of surface-active substances. G.R.S.

Selenium-cadmium pigments for glazes and enamels. K. Azarov and L. Fainrider. *Zhur. Khim. Prom.*, **16** [2] 42–44 (1939).—Best results were obtained with a batch consisting of 61.91 cadmium carbonate, 23.81 sulfur flowers, and 14.28% metalline selenium, the calcining temperature of the pigment being 600°. Pigments containing zinc oxide showed dark brown shades. Enamel coatings containing a bright red pigment showed the best results when fired for a short time. The presence of sulfurous gases in the sagger atmosphere is detrimental to the coloring. The addition of 2 to 6% tin oxide to the frit when grinding has no bad effect on the fusibility of the coating. The addition of electrolytes (NaCl, $MgSO_4$, $CaCl_2$, K_2O, B_2O_3, MgO, and $MgCO_3$) has a very detrimental effect on the coloring, but Glauber's salt has no effect. P.B. & E.S.

PATENTS

Manufacture of lead compounds. O. F. Marvin (Marvin Metals, Inc.). U. S. 2,187,749, Jan. 23, 1940 (June 25, 1935).

Manufacture of pigments. Hugo Querengässer (I. G. Farbenind. A.-G.). U. S. 2,187,822, Jan. 23, 1940 (July 2, 1937).—A process of producing a pigment comprises subjecting an easily water-soluble complex potassium-iron chromate of the approximate composition $7K_2O \cdot 6Fe_2O_3 \cdot 20CrO_3 \cdot 12H_2O$ to a temperature of between about 180° and 220°C. with a corresponding pressure ranging between about 10 and about 20 atm. in an autoclave in the presence of between about 1 and 3 parts its quantity by weight of water and thereupon separating the resulting sparingly water-soluble pigment from the mother liquor.

Manufacture of titanium pigments. British Titan Products Co., Ltd., A. G. Oppegaard, and C. J. Stopford. Brit. 516,369, Jan. 10, 1940 (June 23, 1938).

Treatment of ores. O. F. Marvin (Marvin Metals, Inc.). U. S. 2,187,750, Jan. 23, 1940 (July 31, 1936).

General

Comparative researches upon silicosis: I. G. GERSTEL. *Arch. Gewerbepath. & Gewerbehyg.*, **5**, 249–64 (1934).—G. presents the synthetic structure of mineral dusts involved in his chemical studies upon the lungs of industrial workers dying of dust diseases and his detailed analytic procedure. **II.** *Ibid.*, **6**, 304–48 (1935).—Results of research methods applied to 100 workers for estimates of SiO_2 and TiO_2 occurring in the lung tissues are reported. The results were rigorously tabulated and rechecked. **III, Aluminum oxide content of the lungs of 128 silicosis cases.** *Ibid.*, **8**, 277–316 (1937).—G. points out that this research series does not exhibit the fundamental lacks apparent in previous analytical studies found in the literature, in that (1) a sufficiently large number of cases has been presented, (2) the entire lungs have been reduced to ash, (3) before incineration, every lobe of the lungs was separately explored and recorded for foci of infection as well as foci-free areas, and (4) the analyses undertaken were neither exclusively chemical nor exclusively mineralogical. As the lungs are not the only organs eliminating or converting respired dusts, the lymph nodes, circulatory apparatus, kidneys, and respiratory organs other than the lungs which participate in the severe phenomenon of silicosis were studied. Silicic acid estimates in dust-affected lungs were made, since the SiO_2 significance for silicosis cannot be doubted; the exact circumstances of its behavior in the lungs, however, were not cleared up. G. was the first to show that the mass weight alone of SiO_2 was not the decisive factor in lung injury. Titanic acid estimates were undertaken on purely analytical-technical grounds, Scheid having noted the enormous number of rutile needles in his first lung-ash preparation and Lenzi having reported on titanium dusts. It had been hoped that the TiO_2 analyses might prove the rutile needles important in the origin of dust disease, but their percentage content always remained below 1%. It had also been expected that the aluminum oxide analyses would throw light on the claims of W. R. Jones that sericite, an aluminum silicate, is the real cause of silicosis. G. reviews the basic facts of sericite structure and the chemical reasoning involved. From his experimental procedure he finds no proportional relations existing between SiO_2 and Al_2O_3, as occurring in lung tissues affected by dust, and therefore considers the expectations not justified. Included in the reports of the 128 cases are the chemical data and the pathologic-anatomic findings as well as results of the Al_2O_3 analyses. Fifty of these cases were studied in Part II; 101 new observations are made upon them, taking into account mass values of Al_2O_3 and their earlier content values. The total mass of SiO_2 required estimation as well as the content value in determining the inquiry into sericite. These 128 cases are studied in tabulated groups classified according to the character of the silicosis infection. Cases 1 to 50 are pure silicosis; the ages of the miners, length of time they had worked in the locality, and the clinical aspects and causes of death are given. No tubercular complications or those of any other disease process were shown in the dust foci of this group. One case, a porcelain turner, aged 39, had worked 12 years in Bonn and was an average silicotic with no special distress; he had occasional angina attacks, tonsillary septic abscesses, and multiple lung abscesses. Small individually located dust foci were found in all the lobes of his lungs, with apple-sized nodules in the right upper lobe; some hypertrophy was present in the right heart chamber. Other carefully studied classifications were 78 cases of lung tuberculosis superimposed upon or associated with silicosis, with and without cavities in both lungs or in only one; the data were extremely particularized. Case 128 was another porcelain worker, aged 53, who had worked 23 years in various phases of porcelain fabrication and whose average grade of silicosis was associated with a one-sided cavernous tuberculosis of the lung. Ten results of these researches are summarized. Aluminum values had no relation to SiO_2 values. No relation existed between the severity of the silicosis and the Al_2O_3 content of the lungs, their lobes, or their nodules. Repeated analysis of dust needles found in lung dusts showed that they could not be sericite, either wholly or fractionally. In no case did a definite relation exist between the silicate content of sericite and the SiO_2 masses. Certain marked differences between pure silicotics and silicotuberculous cases are elaborated in respect to individual ways of reacting to dust masses and the sizes of dust foci. In the case of a manganese-ore crusher where the severest lung inflammation was found, no manganese could be detected in the lungs. K.R.

Deficiencies of smoke stacks, their tracing and elimination. R. SALOMON. *Gesundh.-Ing.*, **61** [3] 39 (1938). W.D.K.

Heat insulation. E. A. ALLCUT. *Jour. Can. Ceram. Soc.*, **8**, 4–9 (1939).—In considering heat insulators, the important factors are high resistance to the passage of heat, low first cost, durability, and resistance to fire, moisture, and vermin. A. discusses the advantages and disadvantages of various methods of insulation and points out the discrepancies in the published data on insulating materials. J.G.P.

Plant layout. A. SANKOFF. *Jour. Can. Ceram. Soc.*, **8**, 58–68 (1939).—S. defines what plant layout involves, discusses the most recent layout installed at the Canadian Westinghouse Co., and comments on the equipment installed in both the shop and the laboratory. J.G.P.

Research in industry. FRANK B. JEWETT. *Sci. Monthly*, **48** [3] 195–202 (1939).—Industrial research is of two kinds: (1) work of a fundamental character on problems which, if successfully solved, will be of advantage to the industry at some more or less distant future time, and (2) work concerned with the problems of current operation. This type arises either because the research laboratory is set up to do it or because problems arise in current operation which are beyond the capacity of the operators to cope with. H.E.S.

Steam-heating systems in plants. O. LEPPIN. *Gesundh.-Ing.*, **61** [6] 83 (1938).—Calculations and constructions for central steam-heating systems are described. L. concludes that the central steam-heating system is specially suitable for plant heating and states reasons. W.D.K.

Treatment of injuries from hydrofluoric acid. ZSCHACKE. *Glashütte*, **69** [34] 587–88 (1939).—Every plant working with hydrofluoric acid should be provided with agents for treating even the slightest burn or injury; a solution of milk of lime (calcium hydroxide) should be used to wash the most trivial sprinkling of acid on the skin, and a paste of magnesium oxide and glycerin should be applied. For deep burns a solution of calcium-gluconate-lactobionate for subcutaneous injection is recommended. M.V.C.

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Jour. Soc. Dyers & Colourists
Khim. Referat. Zhur.
Koks & Khim.
Kolloid-Beihefte
Kolloid. Zhur.
Legkie Metally
Manchester Guardian Commercial
Mat. prime ital. imp.
Mech. World & Eng. Record
Metallwaren-Ind. & Galvano-Tech.
Mikrochim. Acta
Mineral. Syr'e
Monatshefte Chem.
Nachr. Ges. Wiss. Göttingen, Jahresber. Geschäftsjahr. Math.-phys. Klasse
Nat. Paint, Varnish & Lacquer Assn., Sci. Sect. Circ.
Norsk Geol. Tids.
Oregon Dept Geol. & Mineral Ind. Bull.
Penna. State Coll., Mineral Ind. Expt. Sta. Bull., Tech. Papers
Physik. Z. Sowjetunion
Platers' Guide
Power & Works Engr.
Proc. Inst. Vitreous Enamellers
Proc. Internat. Conf. Soil Mech. & Foundation Eng.
Quart. Colo. School Mines
Rass. Med. Applicata Lavoro Ind.
Razvedka Nedr.
Rev. Aluminium
Rev. Chim. Ind. [Rio de Janeiro]
Rev. Combustibles Liquides
Rev. Gén. Mat. Color.
Rev. géol.
Rev. Universelle Mines
Rusta-Rayonne
Skláfské Rozhledy
Soils & Fertilizers
Sovet. Foto
Sovet. Geol.
Sovet. Met.
Stavivo
Strade
Suomen Kemistilehti
Tech. Gemeindeblatt
Transit Jour.
Trudy Petrograf. Inst. Akad. Nauk S.S.S.R.
Univ. N. C. Eng. Expt. Sta. Bull.
Usine Belge
Uspekhi Fiz. Nauk
U. S. Tariff Comm., Misc. Ser., Repts. Tariff Information Ser.
Vortrage Emaillierkurs Bergakademie Clausthal. D. Bergiverksztg.
Wärme
Werkstatt & Betrieb
Werkstattstechnik
Year Book Coke Oven Managers' Assn.
Z. angew Mineral.
Zapiski Vserossiiskogo Mineral. Obshchestva
Z. Ges. Natur.
Zitein-Tech-SO
Zprávy České keram. společnosti

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